

THERMODYNAMICS AND STATISTICAL MECHANICS OF
SYSTEMS OF "REACTIVE" COMPONENTS WITH
APPLICATIONS TO STRONG ELECTROLYTES

BY

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... to my parents, for their continual love, encouragement and support throughout the years.

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TABLE OF CONTENTS

		PAGE
	ACKNOWLEDGEMENTS.....	iii
	KEY TO SYMBOLS.....	vi
	ABSTRACT.....	xii
	CHAPTER	
ONE	INTRODUCTION.....	1
TWO	SOLUTION THERMODYNAMICS FOR "REACTIVE" COMPONENTS.....	6
	Introduction.....	6
	Mathematical Basis.....	7
	Construction of Projectors--Material Balance.....	10
	Properties of Solutions.....	11
	Application to Analytic Solution of Groups: UNIFAC and UNIQUAC.....	26
THREE	STATISTICAL THERMODYNAMICS OF "REACTIVE" COMPONENTS IN THE GRAND ENSEMBLE.....	33
	Introduction.....	33
	Components and Species in Complex Systems.....	34
	Grand Ensemble for Systems of "Reactive" Components.....	39
	Composition Fluctuations.....	45
	Complete Reactions.....	54
FOUR	SOLUTIONS OF STRONG ELECTROLYTES.....	61
	Introductions.....	61
	Material Balance Relationships among Salts, Solvents and Ions.....	62
	Formulation in Terms of Direct Correlation Functions.....	68
	Thermodynamic Properties.....	72
	Single-Salt, Single-Solvent System.....	76
	Double-Salt, Single-Solvent Case.....	81
	Single-Solvent, Common Ion Case; Harned's Rule.....	86
FIVE	ELEMENTS OF A MODEL FOR ELECTROLYTIC SOLUTIONS.....	91
	Introduction.....	91
	Primitive Ion Model.....	92

	Calculation of Solution Properties.....	94
	Electrostatic Contributions to Direct Correlation Function Integrals.....	97
	The Form of the Complete Model.....	100
	Preliminary Results.....	101
SIX	AN EXPERIMENT FOR VOLUMETRIC PROPERTIES OF SALT SOLUTIONS AT HIGH PRESSURES.....	104
	Introduction.....	104
	Thermodynamic Basis.....	105
	Experimental Design.....	107
	Operating Procedures.....	112
	Conclusions.....	117
SEVEN	CONCLUSIONS.....	118
APPENDICES		
A	DERIVATIONS OF PRINCIPAL RELATIONS.....	122
B	EXAMPLES OF THE PROJECTION PROCEDURE.....	125
C	EXPRESSIONS FOR THE UNIQUAC AND UNIFAC MODELS.....	139
D	CONSTRUCTION OF MATRICES FOR GENERAL MATERIAL BALANCE.....	143
E	DERIVATIVES WITH RESPECT TO COMPONENT CHEMICAL POTENTIALS.....	146
F	PROJECTION OF INVERSE MOLE FRACTIONS OF LIMITING REACTANTS IN THE LIMIT OF COMPLETE REACTIONS.....	151
G	ALTERNATIVE FORMULATION OF FLUCTUATION PROPERTIES FROM INTEGRALS OF THE RADIAL DISTRIBUTION FUNCTION.....	155
H	INDEPENDENCE OF SALTS.....	160
I	ELECTROSTATIC EXPRESSIONS FOR MULTISALT SYSTEMS.....	164
J	HARD-SPHERE FORMULAE.....	167
	REFERENCES.....	170
	BIOGRAPHICAL SKETCH.....	176

KEY TO SYMBOLS

\underline{A}	species-composition fluctuation matrix
\underline{A}	matrix of composition derivatives of activities for components
$\hat{a}_i, \hat{a}_{o\alpha}$	activity of species i , component α
B_j	name of reactant j
B_{ik}	k th coefficient of activity coefficient expansion for ion i
\underline{C}	matrix of direct correlation function integrals
\underline{C}^o	matrix of integrals of nondivergent portion of direct correlation functions
$C_{\alpha\beta}^o$	salt-salt "direct correlation function" integral
c_{ij}	"centers" direct correlation function
c_{ij}^o	nondivergent portion of direct correlation function
D_{ijk}	k th coefficient in direct correlation function integral expansion for ions i and j
$E_{\underline{N}q}$	energy of system in state defined by $[\underline{N}, q]$
e	magnitude of charge on an electron
\underline{e}_α	unit vector with nonzero α th element
$f^{(1)}$	one-particle density function
$f^{(2)}$	two-particle density function
$G, \Delta G^{\text{MIX}}$	Gibbs free energy, Gibbs free energy change on mixing
\underline{G}	transformation of \underline{A} to Lewis-Randall system variables
\underline{G}'	transformation of \underline{A} to density variables
g_{ij}	pair correlation function
$H, \Delta H^{\text{MIX}}$	enthalpy, enthalpy change on mixing
\underline{H}	matrix of integrals of total correlation functions

h_{ij}	total correlation function
I	ionic strength
$\underline{I}, \underline{I}$	identity matrix, identity matrix in component space
\underline{i}	vector of ones
K_k	equilibrium constant for reaction k
\underline{K}	part of projection matrix for direct correlation functions
k	Boltzmann's constant
\underline{L}	nonsquare matrix related to identity matrix
$M, \Delta M^{\text{MIX}}$	general property, general property change on mixing
m	molality
N	total number of moles or particles
\mathcal{N}	total number of systems in grand ensemble
N_i, N_{α}	number of moles of species i , component α
n, n_o, n_s	number of species, components, solvents
$n_{\underline{N}q}$	number of systems in state defined by $[\underline{N}, q]$
O	lowest order of remaining terms
P	pressure
P_j	name of product species j
\underline{P}	projection matrix of component subspace in species space
$p_{\underline{N}q}$	probability of system being in state defined by $[\underline{N}, q]$
Q	heat of reaction
Q_i	surface parameter for group i
q	set of variables describing quantum state of system
q_{α}	surface parameter for molecule α (UNIQUAC eqns.)
q_{α}	measure of charge strength of salt α (Salt eqns.)
R	gas constant
R_i	volume parameter for group i

R_α	coefficient in test for independence of salts
r	number of reactions
r_α	volume parameter for molecule α
\underline{r}	position vector
$S, \Delta S^{\text{MIX}}$	entropy, entropy change on mixing
S_γ, S_v, S_k	coefficients for Debye-Hueckel limits for mean ionic activity coefficient, partial molar volume, apparent compressibility for single salt system
S_γ^1, S_v^1, S_k^1	same as S_γ, S_v, S_k , except for multisalt system
T	temperature
U	internal energy
U	total interaction energy of groups (UNIFAC eqns.)
\underline{U}	orthogonal left inverse of \underline{W}
U_{ij}	interaction energy of groups i and j
u	molecular total interaction energy
\underline{u}	orthogonal left inverse of \underline{v}
$u_{\alpha\beta}$	interaction energy of molecules α and β
$V, \Delta V^{\text{MIX}}$	volume, volume change on mixing
v, \bar{v}	molar volume, partial molar volume
\underline{W}	material balance matrix
\underline{X}	diagonal matrix of mole fractions
$x_i, x_{o\alpha}$	mole fraction of species i , component α
$\underline{x}_{(\alpha)}^o$	set of mole fractions at reference state of component α
\underline{Y}	constant left inverse of \underline{W}
$y_{o\alpha}$	density-based activity coefficient for component α
\underline{y}	constant left inverse of \underline{v}
\underline{Z}	matrix of stoichiometric constraints in "reactive" system
\underline{Z}_o	constant portion of \underline{Z}

\underline{z}_1	nonconstant portion of \underline{z}
\underline{z}	matrix of charge and stoichiometric constraints on system of strong electrolytes
α	coefficient from Mean Spherical Model for electrolytes
$\alpha_{\beta\gamma}$	Harned coefficient for salt β in solution of salt γ
β	$= 1/kT$, Lagrange multiplier for energy
β_{ij}	physical interaction energy parameter
γ	mole fraction based activity coefficient
γ_m	molality based activity coefficient
$\delta(\underline{r})$	Dirac delta function
δ_{ij}	Kroniker delta
ϵ, ϵ_1	dielectric constant of solution, solvent
ζ	quantity for hard sphere contributions
η_k	weighted average of ionic size parameters
θ_i	surface fraction of group i
θ_{ij}	local surface fraction for groups i and j
$\theta_i^{(\alpha)}$	surface fraction of group i in molecule α
θ_α	surface fraction of molecule α
θ_k	Lagrange multiplier for constraint k
$\theta_{\alpha\beta}$	local surface fraction for molecules α and β
κ	inverse Debye length
κ_T, κ_1	isothermal compressibility of solution, solvent
λ_α	absolute activity of component α
$\mu_i, \mu_{o\alpha}$	chemical potential of species i , component α
\underline{v}	matrix of stoichiometric coefficients
ξ	intensive extent of reaction
ρ, ρ_o	total density of species, components

$\rho_i, \rho_{o\alpha}$	density of species i , component α
$\rho_i^{(1)}$	ensemble-averaged one-particle density
$\rho_{ij}^{(2)}$	ensemble-averaged two-particle density
σ_i	size parameter for species i (hard sphere diameter)
$\tau_{\alpha\beta}$	interaction parameter for molecules α and β
Φ_k	apparent compressibility for multisalt systems
ϕ_i	volume fraction for group i
ϕ_k	apparent compressibility for single-salt systems
ϕ_α	volume fraction for molecule α
ψ_{ij}	interaction parameter for groups i and j
Ω	volume of orientation space
$\underline{\omega}$	vector of Euler angles

Subscripts

c	chemical contribution to ΔG^{MIX}
C	set of components
D	set of dependent species
i, j, \dots	species or group quantity
$k,$	reaction number
L	set of limiting reactants
n	normalized quantity
o	properties in component space
P	set of products
p	physical contribution to ΔG^{MIX}
S	set of solvents
α, β, \dots	component or molecular quantity

Superscripts

E	excess property
elec	electrostatic contribution
f	final state for integration of thermodynamic properties
hs	hard-sphere property
(ℓ)	reaction set in sequential reactions
MIX	mixture property
T	transpose of vector or matrix

Special Symbols

$\underline{}$ (as in \underline{A})	vector or matrix quantity
$\overline{}$ (as in \overline{v}_i)	partial molar property
$\langle \rangle$ (as in $\langle N \rangle$)	ensemble average
$^{\circ}$ (as in $\underline{\mu}^{\circ}$)	reference or standard state
$^{\infty}$ (as in $\overline{v}_i^{-\infty}$)	infinite dilution value
\pm (as in m_{\pm})	mean ionic property
$\underline{\ln}$ (as in $\underline{\ln \lambda}$)	vector of logarithms of a quantity

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The task of quantitatively describing physical properties of solutions, whether for use in engineering design and optimization, or for understanding natural processes, grows increasingly difficult as more accuracy is demanded and more complex systems are studied. To meet these demands, engineering thermodynamics now looks more thoroughly into the intermolecular forces in a solution, and rely more on the theoretical, rather than empirical, bases for their quantitative descriptions. This molecular basis is particularly important when "reactive" systems--those systems where component molecules interact so as to form different chemical species--are considered. This work develops a statistical mechanical solution theory for such systems, examining the constraints caused by their "reactive" nature, and a model which may be applied to correlate and predict their thermodynamic properties.

The thermodynamic consistency requirements of models for "reactive" solutions are expressed. These are used to formulate a procedure, using matrix projections, which builds these requirements into the solution model. The statistical mechanics of such a solution in the grand canonical ensemble is explored in light of the "reactive" constraints and the consistency requirements. By using the projection procedure mentioned above, the derivative, or fluctuation, properties of the components in a general "reactive" system are related to equilibrium relations and molecular correlation functions.

The case of total dissociations as the only "reactions" in the solution is explored, with specific applications to strong electrolytes. First, the singularities of the long range interactions are shown to be removed by the projection procedure. Then a model is formulated based on a composite of hard-sphere and charge effects. This model, though presently not complete, shows considerable promise in correlating the properties of salt solutions. An experimental apparatus for volumetric behavior of liquids was completed and methods are described for using data from it to evaluate the parameters in the solution model, as well as develop a better understanding of density effects in electrolyte solutions.

CHAPTER 1 INTRODUCTION

Design and optimization of industrial processes and equipment, as well as quantitative understanding of natural or biological processes, require quantitative descriptions of the physical properties of the components of those systems. A very important need is the correlation and prediction of P-V-T- \underline{x} relationships and phase equilibria in multicomponent liquid systems. Meeting this need can be quite difficult, especially if there are complicated intermolecular interactions or tight constraints on accuracy. The situation is complicated further in "reactive" systems, where the relative amounts of the species in a given system are constrained by equilibrium conditions or stoichiometry. These "reactive" systems include, in general, solvation, dissociation and association -- including processes such as micellization or ionization of salts. A large number of real systems exhibit this "reactive" nature, although it may proceed to such a small degree that it is negligible. In other situations, however, the additional species and constraint relations contribute appreciably to the solution properties. Although specific types of systems have been treated previously (e.g. Renon and Prausnitz, 1967), there has not been a general approach to these systems which could serve as a guideline for the consistent use of solution models.

Solutions involving electrolytes are a class of "reactive" systems which are of particular interest. Electrolytes appear in geological liquid systems (oil reservoirs, geothermal energy sources), in systems of biological interest (e.g. in active transport in membranes and in using salts to separate proteins), and have important applications to industrial systems (extraction, distillation and reverse osmosis). These systems have an additional complication, though, because of the presence of long-range coulombic interactions in addition to equilibrium and stoichiometric constraints.

Statistical mechanical approaches have been successful for many non-"reactive" systems, as well as some specific "reactive" systems (Friedman and Ramanathan, 1970). A recent approach using fluctuation solution theory (Mathias and O'Connell, 1980a,b) has shown application for gases dissolved in various solvents at high pressures. This procedure is based on molecular correlation functions and works particularly well in systems which contain components of very different natures. Hence, it should be useful for salt solutions.

This work aims, firstly, to treat "reactive" systems in a manner that is applicable to any system, and so to present a general and unifying thermodynamic framework in which correlations can be consistently developed. This framework is then applied to the above statistical mechanical method to develop a formalism for expressing the properties of "reactive" solutions in terms of these molecular correlation functions. Finally, this formalism is applied to solutions of strong electrolytes and a solution model is examined.

Chapter two develops the classical thermodynamics of "reactive" systems. There, the "reactive" nature is defined mathematically in terms of the material balance (stoichiometric) relations and intensive extents of reactions. The total amounts of chemical species in a system are related to the amounts of components (where the components each represent a degree of freedom in composition) by a matrix relation which is, in effect, a projection of the species space into the component subspace. The projection operators are completely defined by stoichiometry and equilibria, and are used to relate solution properties in terms of species to the required solution properties in terms of components. . These relations also show restrictions which must be placed on solution models for such systems, and two specific examples are detailed.

Chapter three begins with the definition of a grand ensemble with overall constraints on the mole numbers of the species. It then derives a solution theory based on total and direct correlation functions, between species that yields component properties. This functionality is important because, although the ensemble-averaged species composition vector must lie in the component subspace, this is not necessary for the species composition vectors for any of the systems in the ensemble. The chapter then gives the component density derivatives of the component activities in terms of the reaction extents and the integrals of the species direct correlation function integrals. Lastly, a detailed analysis of the matrix equations for a system which undergoes complete dissociations is given, and the matrices are shown to collapse to a very simple form.

Chapter four considers a specific case of complete dissociation-- a system of strong electrolytes dissolved in a non- "reactive" solvent. First, it reformulates the results of chapter three using dimensionally smaller matrices, explicitly accounting for the absence of the undissociated salts. In this formulation, it is shown that the long-range portions of the direct correlation function integrals (which diverge in integration) are exactly removed by the projections. Isothermal compressibilities, partial molar volumes and composition derivatives of the activity coefficient are given in terms of special integrals of the ion-ion, ion-solvent, and solvent-solvent direct correlation functions, and the Debye-Hueckel limits of these properties are given. Two specific cases are examined, the simplest case of one salt and one solvent and the case of two salts with a common anion. The latter example gives the Harned coefficients in terms of the correlation function integrals.

Chapter five deals with the development of a model for the electrolyte solutions. Results of previous theory and experimental results are used to determine the type of model to be used. The direct correlation function between molecules i and j is given:

$$C_{ij}(r) = C_{ij}^{hs}(r) + \{C_{ij}(r) - C_{ij}^{hs}(r)\}$$

where the terms superscripted hs are the direct correlation functions for a system of hard spheres. The bracketed term, which corresponds primarily to electrostatic effects, is approximated by a composite

expression, based on a low-density expansion such as the mean spherical model, with correction to the proper infinite dilution properties including hydration of ions. The model is formulated in terms of several universal (not salt dependent) constants, and functions of ionic size, charge and density. Some rough, preliminary calculations are given.

Chapter six examines an experimental method by which volumetric behavior of salt solutions can be determined over a sizeable range of pressures and temperatures. The range of operation allows the effects of total density and composition on free energies to be examined individually by allowing available activity data at low pressures to be extended to higher pressures (at constant density). It also provides a basis for determining the model parameters for the electrolyte direct correlation functions. The design and operation of this experiment are described.

Finally, further applications of the results of this work, as well as suggestions for extensions, are given.

CHAPTER 2

SOLUTION THERMODYNAMICS FOR "REACTIVE" COMPONENTS

Introduction

Fundamental to the development of thermodynamic properties is the mathematical rigor that yields basic relationships such as Maxwell relations (Van Ness, 1964), identification of partial derivatives (e.g., heat capacities), and Legendre Transformations (Beegle et al., 1974). Provided the requirements of the specification of thermodynamic state are met, natural phenomena appear to follow all the mathematical consequences of the First and Second Laws and subsequent definitions, even for systems of many components and modes of interaction with the surroundings (Redlich, 1968).

The most complex systems to deal with are those involving chemical reactions because the compositions of the species are connected at equilibrium. In regard to this fact, the purpose of this chapter is to display a mathematical formalism for expressing the solution thermodynamic properties of mixtures made of components which can react to form additional species. Their concentrations can be related through equilibrium constants or there can be complete dissociation. The particular situations of current interest include electrolytes, both strong and weak, the "chemical theory" of solutions (Prausnitz, 1969) and the "solution of groups" method for activity coefficients (Derr and Deal, 1968, 1969, 1973; Fredenslund et al., 1977a). Our motivation is to

provide a degree of unification not heretofore attempted so that derivations can be streamlined and any potential inconsistencies can be avoided, particularly in the development of molecular and statistical thermodynamic theories and correlations. The results obtained for the first two cases are the same as found previously. They have been extended to a more complete set of thermodynamic properties. In the solution of groups method we have found precisely how analytical solution of groups methods such as UNIFAC (Fredenslund et al., 1977b) yield different results from the molecular equation upon which they are based (e.g., UNIFAC from UNIQUAC, Abrams and Prausnitz, 1975).

The results of this analysis form the framework for the more detailed analysis of the statistical mechanics of solutions of "reactive" components, and in particular for the modelling of properties of solutions of strong electrolytes, which are the subjects of subsequent chapters.

Mathematical Basis

The mathematical situation is one in which the thermodynamic functions of interest (enthalpy, entropy, activities, etc.) are most conveniently expressed in terms of a set of variables related to the number of moles of species, N , or their mole fractions, x , but actually must be functions of the set of independent values related to the number of moles of the original components, N_0 , or their mole fractions, x_0 . The fact that the number of independent variables in the former case is different from the number in the latter case requires that the functions be projected from one space to another.

Figure 1 is a graphic representation of the projection process. Here, we treat the case of three species, with two independent mole fractions, in a two component system with only one independent mole fraction. The surface represents the values of the thermodynamic property, M , for all values of the species fractions satisfying

$$\sum_i x_i = 1$$

However, the "allowable" compositions of species are controlled by the stoichiometry of the "reaction" system. These values are constrained to the projection of the species fractions, which here is a line in the base plane. The attainable values of the system thermodynamic property, M_0 , are the projection of M , the curve formed by the intersection of its surface with the vertical plane containing the line of "allowed" species fractions. In multicomponent-multispecies systems the system thermodynamic property values will be found in the intersection of the property surface in species space and a hypersurface for the allowable species fractions. Our purpose is to establish a general procedure to obtain this intersection. The mathematical operators for this procedure in the present case can be straightforwardly defined and are easily used as standard matrix manipulations.¹

This method has been implicitly used in a wide variety of situations such as electrolyte solutes, the "chemical theory" of solutions and "analytical solution of groups" correlations. While the

¹In certain statistical thermodynamic developments the method is more complex but represents the only technique we know to remove certain apparent divergences (Perry et al., 1980a)

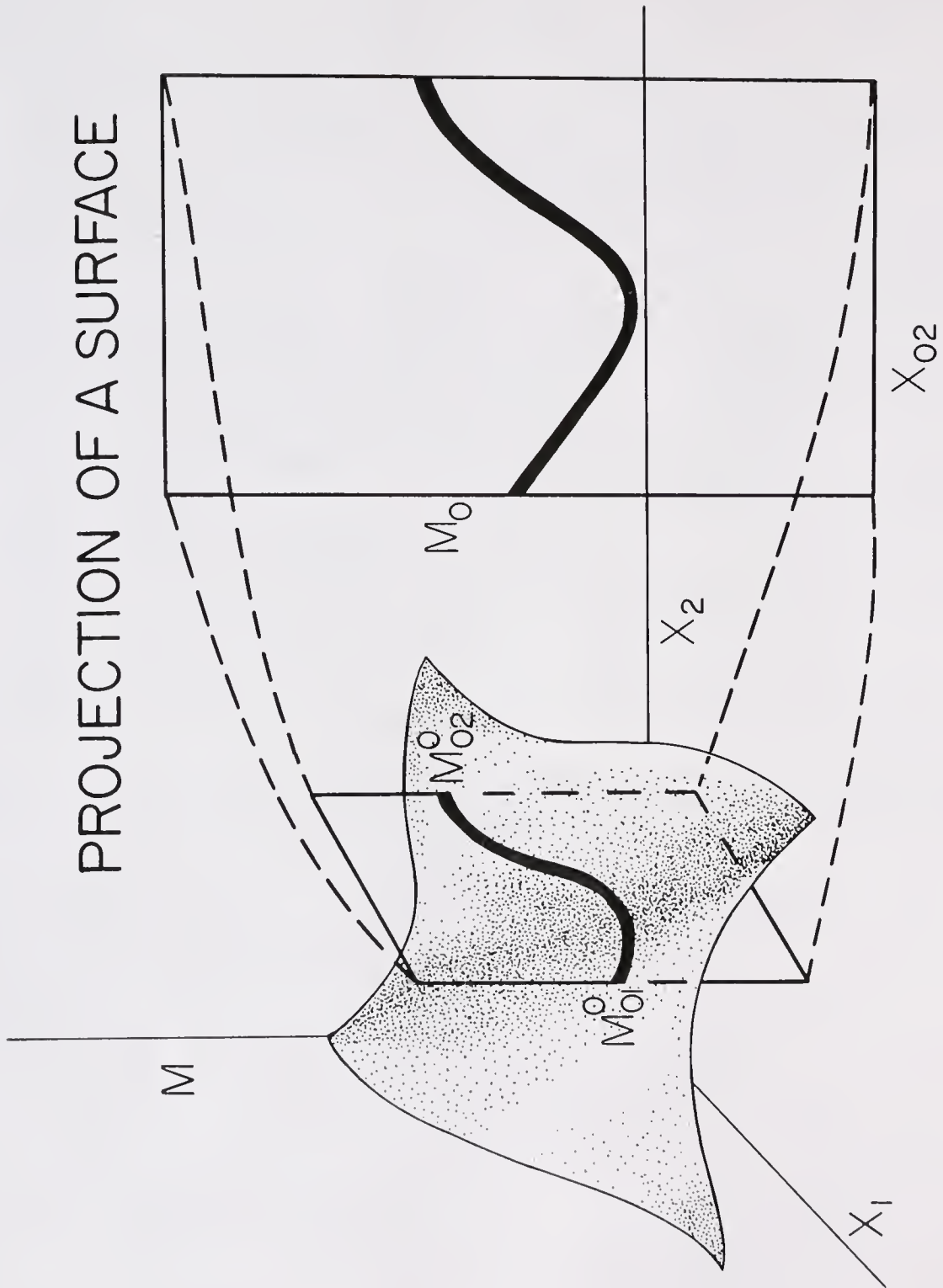


Figure 1. Projection of a thermodynamic property surface.

number of "new" results is not large, our objective is to unify apparently diverse approaches and present a single procedure for use in all problems where the properties of a solution are to be obtained from model expressions for the properties of the species.

Construction of Projectors -- Material Balance

We will begin by examining a closed system at fixed T and P made from the mixing of n_0 components, with the mole numbers of the components given by the vector \underline{N}_0 . This system may now undergo successive associations, dissociations or reactions leading to an equilibrium system of n species, with mole numbers given by the vector \underline{N} . In order to relate the species vector \underline{N} to the component vector \underline{N}_0 we will use a process which is chosen for mathematical convenience and is not intended to reflect the chemical evolution of the system. The general development is given in Appendix A; two complete examples are given in Appendix B.

The general result is

$$\underline{N} = \underline{W} \underline{N}_0 \quad (2-1)$$

where \underline{W} (defined in Appendix A) is a matrix involving the stoichiometric coefficients and extents of reaction of the independent reactions which change components into species.

The importance of this relationship lies in the fact that \underline{N}_0 has n_0 degrees of freedom, and since the extents of reaction are functions of \underline{N}_0 only (at constant T and P), \underline{N} also has only n_0 degrees of freedom. However, it is in a space with n degrees of freedom. Thus \underline{W} is a projector from a space of dimension n_0 into a space of dimension n .

As shown below, use of this and related matrices allows us to project, without any loss of information, expressions for thermodynamic properties into the desired n_0 -space that are naturally written in n -space. It must be emphasized that the apparently simple relationship of equation (2-1) contains a considerable number of subtleties. The next few sections show the ramifications that this relation has on the thermodynamics of solutions. An example involving 2 components, 4 species, and 2 reactions is given in Appendix B.

Properties of Solutions

Partial Molar Properties

We will now see how solution properties, especially partial molar properties, are projected using the \underline{W} matrix defined above. First, assuming our mixture to have reached equilibrium and for T and P to be constant, we know

$$\left. dG \right|_{T,P} = 0 \quad \text{where} \quad G = \underline{N}^T \underline{\mu} \quad (2-2)$$

$$\text{and} \quad \mu_i = \left. \frac{\partial G}{\partial N_i} \right|_{T,P,N_{j \neq i}}$$

Since G is really only a function of the \underline{N}_0 with T and P constant, we can use Euler's theorem to also write

$$G = \underline{N}_0^T \underline{\mu}_0 \quad \text{with} \quad \mu_{0\alpha} = \left. \frac{\partial G}{\partial N_{0\alpha}} \right|_{T,P,N_{0\beta \neq \alpha}} \quad (2-3)$$

Reaction equilibrium can be expressed as

$$\underline{v}^T \underline{\mu} = \underline{0} \quad (2-4)$$

where \underline{v} is an $n \times r$ matrix with $(v)_{ik}$ being the stoichiometric coefficient of species i in reaction k and r being the total number of independent reactions (see Appendix H). Then, after some manipulation (see Appendix A), we obtain

$$\underline{W}^T \underline{\mu} = \underline{\mu}_0 \quad (2-5)$$

A consequence of this is the well-known result that for any component α which is also found as a species in the solution,

$$\mu_{\alpha} = \mu_{0\alpha} \quad (2-6)$$

or

$$\left. \frac{\partial G}{\partial N_{\alpha}} \right|_{T,P,N_{j \neq \alpha}} = \left. \frac{\partial G}{\partial N_{0\alpha}} \right|_{T,P,N_{0\beta \neq \alpha}} \quad (2-7)$$

Then, since all the partial molar quantities of interest are linear combinations of $\underline{\mu}_0$ (or $\underline{\mu}$) and its derivatives, all of the other partial molar properties of components are also unchanged by the reactions. That is, for a general partial molar quantity (M = volume, energy, entropy, log of fugacity, etc.) we have:

$$\bar{M}_{0\alpha} = \bar{M}_{\alpha} \quad \alpha = 1, \dots, n_0 \quad (2-8)$$

Equation (2-7) is surprisingly simple since the derivative in n_o -space is complex. However, as long as M is a linear combination of G and its derivatives, equation (2-8) holds because of the linearity of (2-2).

This is valuable in the chemical theory of solutions.

Further, these same linear relations, when applied to equation (2-4) also yield

$$\underline{v}^T \underline{M} = 0 \quad (2-9)$$

Mixing Properties

For mixing properties, the differences in reference states of the components and species appear. Looking, for example, at the change in Gibbs free energy on mixing,

$$\Delta G^{\text{MIX}} = \underline{N}^T \underline{\Delta G}^{\text{MIX}} = \underline{N}^T \underline{\mu} - \underline{N}^T \underline{\mu}^o \equiv RT \underline{N}^T \underline{\ln \hat{a}} \quad (2-10)$$

while

$$\Delta G_o^{\text{MIX}} = \underline{N}_o^T \underline{\Delta G}^{\text{MIX}} = \underline{N}_o^T \underline{\mu}_o - \underline{N}_o^T \underline{\mu}_o^o \equiv RT \underline{N}_o^T \underline{\ln \hat{a}_o} \quad (2-11)$$

where the relationship between $\underline{N}^T \underline{\mu}^o$ and $\underline{N}_o^T \underline{\mu}_o^o$ depends upon the choice of component reference state composition. From equation (2-5), equations (2-10) and (2-11) and the Gibbs-Duhem equation

$$\underline{\Delta G}_o^{\text{MIX}} = \underline{W}^T \underline{\Delta G}^{\text{MIX}} - (\underline{\mu}_o^o - \underline{W}^T \underline{\mu}_o^o) \quad (2-12a)$$

In terms of the initial components, the two forms for the chemical potential are

$$(\underline{\mu}_o)_\alpha \equiv \mu_{o\alpha} = (\underline{\mu}_o^o)_\alpha + R T \{ (\underline{\ell n x})_o_\alpha + (\underline{\ell n \gamma})_o_\alpha \} \quad (2-13a)$$

$$= (\underline{W}^T \underline{\mu}^o)_\alpha + R T \{ (\underline{W}^T \underline{\ell n x})_\alpha + (\underline{W}^T \underline{\ell n \gamma})_\alpha \} \quad (2-13b)$$

Equation (2-13a) is the normal form for $\mu_{o\alpha}$. Equation (2-13b) is the general expression for this quantity in terms of the species variables: it is applicable to all cases regardless of the reference states chosen.

The same relationships exist for all partial molar properties since they can all be found by linear operations (including differentiation and multiplicative functions) on the chemical potentials. Thus for

$$\bar{M}_i = f(\mu_i)$$

then

$$\underline{\Delta M}_o^{MIX} = \underline{W}^T \underline{\Delta M}^{MIX} - f(\underline{\mu}_o^o - \underline{W}^T \underline{\mu}^o) \quad (2-12b)$$

Figure 2 shows a representation of the projection method for ΔM^{MIX} when the reference state composition for component 1 is pure, $x_{o1}^o = 1$, and "infinite dilution" (or a hypothetical state of pure component whose fugacity is Henry's constant) for the others. Such a choice is made with electrolytes and supercritical substances. Here, it has been assumed that species 2 and 3 are contained only in component

PROJECTION WITH "INFINITE DILUTION" REFERENCE STATES

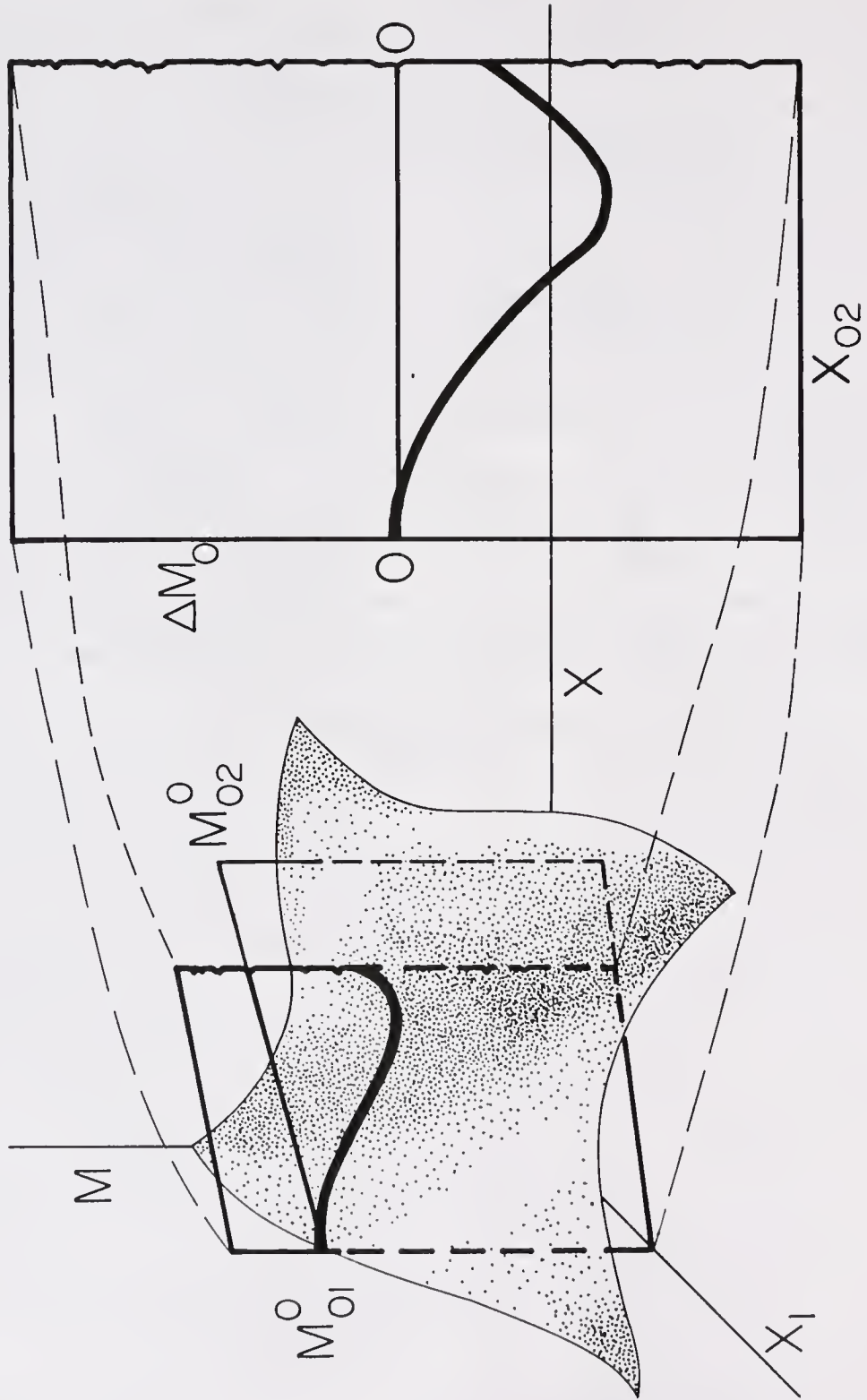


Figure 2. Projection with "infinite dilution" reference states.

2, so an ideal solution occurs when $x_{o2}^o = x_2^o = x_3^o = 0$. The value of \bar{M}_{o2} in the reference state is \bar{M}_{o2}^∞ which corresponds to no particular pure species value. It is merely the extrapolation to (hypothetical) pure component 2 ($x_{o2}^o = 1$) of the tangent to the line of the projection at x_{o1}^o . The line of extrapolation is the ideal solution line which becomes horizontal in the plot of ΔM_o^{MIX} vs. x_{o2} . Note that we have terminated the plane at an arbitrary point where the physical state might change due to a solid phase or a critical point being encountered. The last term in equation (2-12b) would be the difference between the line shown and the line of intersection of the plane connecting all of the $M_i^o = \lim_{x_i \rightarrow 1} M$ and the (vertical) stoichiometric plane.

These two lines need not be parallel.

On the other hand, Figure 3 indicates the results for a case where the reference states for the components are pure component. Thus $x_{o1}^o = 1$ and $x_{o2}^o = 1$. This graph of ΔM_o^{MIX} vs. x_{o2} is more likely to show a sign change even though the surface in species space might not indicate such behavior when examined by itself. Slight undulations of the surface can yield sigmoidal projections.

Among the many ways of dealing with equations (2-13), several common ones have been chosen. The method of Prigogine and Defay (1954) has the same reference state for any initial component which may also be present as a species in the solution. That is

$$\mu_{o\alpha}^o = \mu_\alpha^o \quad \alpha = 1, \dots, n_o \quad (2-14a)$$

PROJECTION WITH PURE REFERENCE STATES

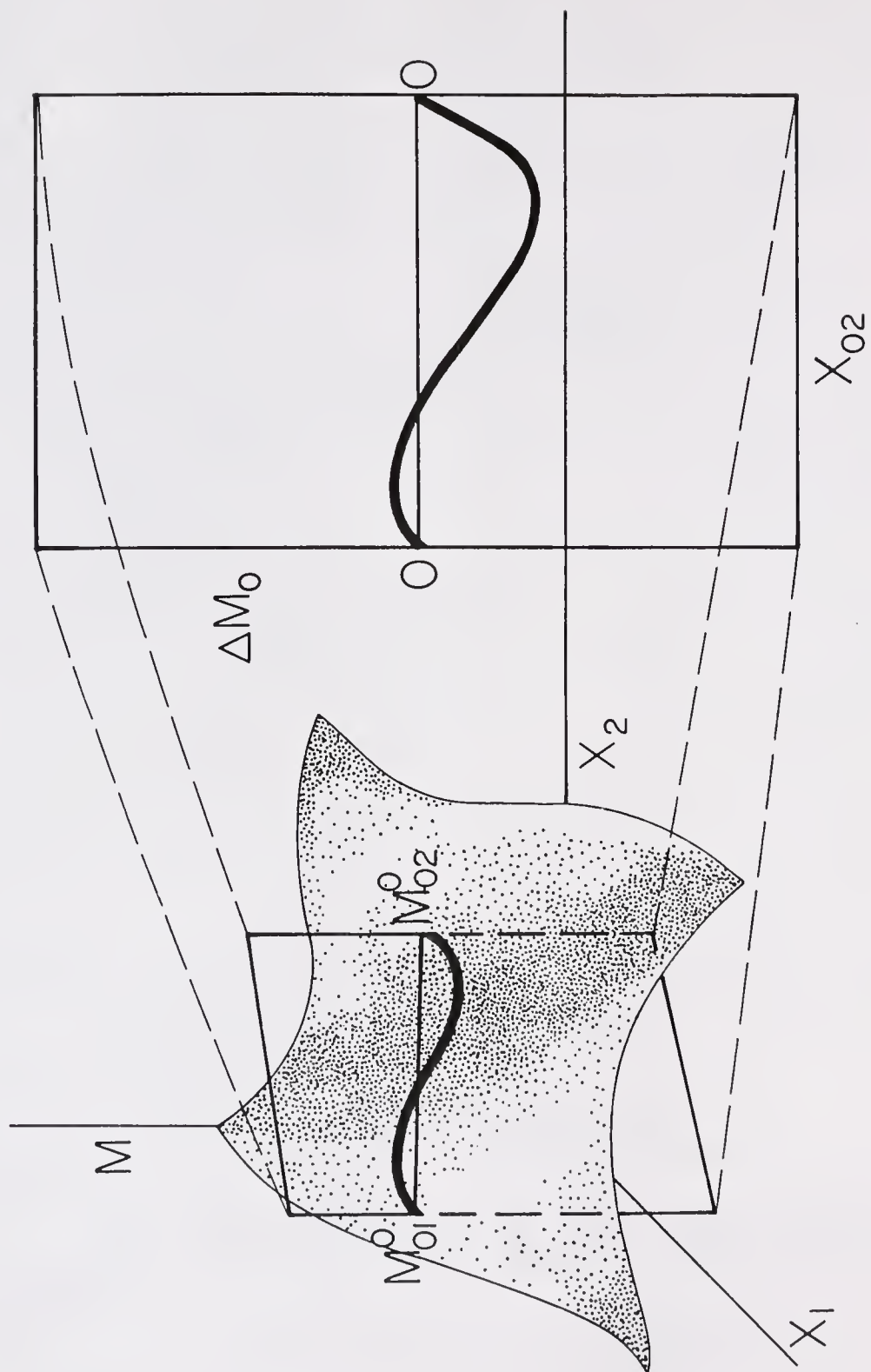


Figure 3. Projection with pure component reference states.

$$\underline{\mu}_O^O = \underline{L}^T \underline{\mu}^O \quad (2-14b)$$

This is most useful for solutions where the components are considered pure, but react when mixed with other components (e.g. solvation). It is this case, and only this one, for which the most common relation holds

$$\ln x_{O\alpha} \gamma_{O\alpha} = \ln x_{\alpha} \gamma_{\alpha} \quad (2-14c)$$

A second choice is the case where \underline{W}^T is independent of composition. It is normally used when complete reactions are assumed. Examples include strong electrolytes and solutions of groups, which are discussed in detail later. Here, it is assumed that

$$\underline{\mu}_O^O = \underline{W}^T \underline{\mu}^O \quad (2-15a)$$

with

$$\underline{\ln x}_O + \underline{\ln \gamma}_O = \underline{W}^T \underline{\ln x} + \underline{W}^T \underline{\ln \gamma} \quad (2-15b)$$

In such a case \underline{W} is a constant and there can be no successive reactions so that the upper $n_O \times n_O$ elements of \underline{W} are either unity (unreacting solvents) or either zero or ratios of stoichiometric coefficients (completely reacting components) and the lower $(n-n_O) \times n_O$ elements form the matrix \underline{v} . It is thus more convenient to reformulate the expressions in terms of a matrix which has only nonzero rows as discussed below.

Finally, there are cases in which the species standard states bear no relation to the component standard states. An example of this is an associating substance which even when "pure" is made up of a number of species (Figure 3 is an example of such a system). Then the full equations (2-13) must be used. The technique here is to subtract equation (2-13b) for the component reference state from the expression at the solution conditions. For equation (2-13b) this is written as

$$\begin{aligned} \underline{\mu}_o - \underline{\mu}_o^o &= \underline{W}^T \{ \underline{\mu}^o + \underline{\Delta G}^{\text{MIX}} \} - \lim_{\underline{x}_o(\alpha)} \underline{W}^T \{ \underline{\mu}^o + \underline{\Delta G}^{\text{MIX}} \} \\ &= \underline{W}^T \underline{\Delta G}^{\text{MIX}} - \lim_{\underline{x}_o(\alpha)} \underline{W}^T \underline{\Delta G}^{\text{MIX}} + [\underline{W}^T - \lim_{\underline{x}_o(\alpha)} \underline{W}^T] \underline{\mu}^o \end{aligned} \quad (2-16a)$$

where $\underline{x}_o(\alpha)$ is the vector of species mole fractions at the reference state of component α . In the case of systems where the components are present as species and the model for $\underline{\Delta G}^{\text{MIX}}$ includes all the contributions to ΔG_o^{MIX} , this becomes

$$\underline{\mu}_o - \underline{\mu}_o^o = \underline{L}^T \underline{\Delta G}^{\text{MIX}} - \underline{L}^T \lim_{\underline{x}_o(\alpha)} \underline{\Delta G}^{\text{MIX}} \quad (2-16b)$$

If the standard state for species is chosen such that $(\underline{x}^o)_i = 1$ and the phase is the same as that of the solution, the last term in equation (2-14) removes any composition independent terms arising from the differences in phase or structure in the expression chosen for $\underline{\Delta G}^{\text{MIX}}$. An example of this procedure is given in Appendix B.

Often, the reactions are described in terms of equilibrium constants which are defined as

$$\underline{\ell_{nK}} \equiv -\underline{\nu}^T \underline{\mu}^O / RT \quad (2-17a)$$

which, with equations (2-4) and (2-10), yields

$$\underline{\ell_{nK}} = \underline{\nu}^T \underline{\ell_{n\hat{a}}} \quad (2-17b)$$

Equations (2-1) and (2-17a) allow us to rearrange (2-12) to a relation explicit in the extents of reaction and equilibrium constants. The general result is given in Appendix A. Equation (A-11) for one set of reactions (no sequential reactions) reduces to

$$\underline{\bar{W}}^T \underline{\Delta G}^{MIX} = \underline{\Delta G}_O^{MIX} + RT \underline{\xi}^T \underline{\ell_{nK}} \quad (2-18a)$$

This relation, or equation (A-11), can be used in place of equation (2-12a) in any of the above derivations, including an alternative to equation (2-16a).

The other mixing properties have similar relationships. For one set of reactions, we can in general write

$$\bar{M}_i = f(\mu_i)$$

where f is a linear operator (including derivatives and multiplicative functions). Then

$$\underline{W}^T \underline{\Delta M}^{\text{MIX}} = \underline{\Delta M}_O^{\text{MIX}} + R \underline{\xi}^T f(T \underline{\ell n K}) \quad (2-18b)$$

For example, using standard operations on equation (2-15) for definitions of μ_i^0 not functions of pressure

$$\underline{W}^T \underline{\Delta H}^{\text{MIX}} = \underline{\Delta H}_O^{\text{MIX}} + R \underline{\xi}^T \frac{d \underline{\ell n K}}{d 1/T} \quad (2-18c)$$

$$\underline{W}^T \underline{\Delta V}^{\text{MIX}} = \underline{\Delta V}_O^{\text{MIX}} \quad (2-18d)$$

$$\underline{W}^T \underline{\Delta S}^{\text{MIX}} = \underline{\Delta S}_O^{\text{MIX}} - R \underline{\xi}^T \frac{d(T \underline{\ell n K})}{dT} \quad (2-18e)$$

and so on. Thus equation (2-18c) gives the familiar relation for the heat effect associated with mixing the components expressed in terms of the activities of the species and the equilibrium constant

$$\begin{aligned} Q = \Delta H_O^{\text{MIX}} &= \underline{N}_O^T \underline{\Delta H}_O^{\text{MIX}} = \underline{N}_O^T \underline{W}^T \left. \frac{\partial \underline{\mu}/T}{\partial 1/T} \right\rangle_{P,N} - R \underline{N}_O^T \frac{d \underline{\ell n K}}{d 1/T} \\ &= R \underline{N}_O^T \left. \frac{\partial \underline{\ell n \gamma}}{\partial 1/T} \right\rangle_{P,N} - R \underline{N}_O^T \underline{\xi}^T \frac{d \underline{\ell n K}}{d 1/T} \end{aligned} \quad (2-19)$$

If the temperature variation of the activity coefficients is ignored, the result is that usually found for reactions in the standard state. This relation is also appropriate for the chemical theory of solutions.

Excess Properties

Excess properties differ from mixing properties because an additional composition term appears in some excess properties (G^E, A^E, S^E). Using the usual notation we have for component values:

$$G_o^E/RT = \frac{N_o^T \ell_{n\hat{a}}}{N_o} - \frac{N_o^T \ell_{nx}}{N_o} \equiv \frac{N_o^T \ell_{n\gamma}}{N_o}$$

$$- S_o^E/R = \frac{N_o^T}{N_o} \left. \frac{\partial T \ell_{n\hat{a}}}{\partial T} \right|_{P, N_o} + \frac{N_o^T \ell_{nx}}{N_o} \quad \text{etc.}$$

For the species values, however, we have

$$G^E/RT = \underline{N}^T \underline{\ell_{n\hat{a}}} - \underline{N}^T \underline{\ell_{nx}} \equiv \underline{N}^T \underline{\ell_{n\gamma}}$$

$$- S^E/R = \underline{N}^T \left. \frac{\partial T \underline{\ell_{n\hat{a}}}}{\partial T} \right|_{P, \underline{N}_o} + \underline{N}^T \underline{\ell_{nx}}$$

Use of equation (2-5) on the above relations gives

$$\underline{\overline{G}}_o^E = \underline{W}^T \underline{\overline{G}}^E - RT(\underline{\ell_{nx}}_o - \underline{W}^T \underline{\ell_{nx}}) - (\underline{\mu}_o^o - \underline{W}^T \underline{\mu}^o) \quad (2-20a)$$

$$= \underline{W}^T \underline{\Delta G}^{\text{MIX}} - RT \underline{\ell_{nx}}_o - (\underline{\mu}_o^o - \underline{W}^T \underline{\mu}^o) \quad (2-20b)$$

For the case of equations (2-14), the activity coefficients become

$$\ell_{n\gamma}_{o\alpha} = \ell_{n\gamma}_{\alpha} + \ell_{n(x_{\alpha}/x_{o\alpha})} \quad (2-21a)$$

For the case of equations (2-15) the relation is

$$\ln \gamma_{o\alpha} = (\underline{W}^T \underline{\ln \gamma})_{\alpha} + (\underline{W}^T \underline{\ln x})_{\alpha} - \ln x_{o\alpha} \quad (2-21b)$$

For the case of equation (2-16) the relation is

$$\ln \gamma_{o\alpha} = \{ (\underline{L}^T \underline{\Delta G}^{\text{MIX}})_{\alpha} - (\underline{L}^T \lim_{\underline{x}_o(\alpha)} \underline{\Delta G}^{\text{MIX}})_{\alpha} \} / RT - \ln x_{o\alpha} \quad (2-22)$$

In terms of the equilibrium constants of a single set of reactions,

$$\underline{W}^T \underline{G}^E = \underline{G}_o^E + RT \underline{\xi}^T \underline{\ln K} + RT (\underline{\ln x}_o - \underline{W}^T \underline{\ln x}) \quad (2-23a)$$

or in terms of activity coefficients

$$\underline{W}^T \underline{\ln \gamma} = \underline{\ln \gamma}_o + \underline{\xi}^T \underline{\ln K} + \underline{\ln x}_o - \underline{W}^T \underline{\ln x} \quad (2-23b)$$

Finally, for the entropy,

$$\underline{W}^T \underline{S} = \underline{S}_o^E + R \underline{\xi}^T \left. \frac{\partial T \underline{\ln K}}{\partial T} \right|_{P, \underline{N}_o} + R (\underline{\ln x}_o - \underline{W}^T \underline{\ln x}) \quad (2-23c)$$

Of course, for successive reactions, $\underline{\xi}^T \underline{\ln K}$ must be replaced with the general expression.

Unfortunately, due to the presence of the logarithm, the excess function expressions do not have the kind of cancellation there is for the partial molar and mixing properties.

An apparent simplification of equations (2-20) is normally made for electrolyte solutions. A set of components is defined for which

$$\underline{\ln x}_{\pm} \equiv \underline{W}_n^T \underline{\ln x} \quad (2-24)$$

where \underline{W}_n^T is \underline{W}^T with its elements suitably normalized.

Then,

$$\underline{\ln \gamma}_{\pm} \equiv \underline{W}_n^T \underline{\ln \gamma} \quad (2-25)$$

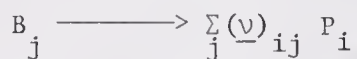
However, this results in a set of components which are not those which could be used to make up the system. That is,

$$x_{\pm\alpha} \neq x_{o\alpha} \equiv N_{o\alpha} / \sum_{\beta=1}^{n_o} N_{o\beta}$$

This difference requires extra care in expressing the properties of partially dissociating systems (weak electrolytes).

Complete Dissociation

An important special case of the above formulae, applying especially to strong electrolytes and "solutions of groups" methods, is the case of complete dissociation. Here, we simplify \underline{W} by eliminating rows of zeros, making it into a matrix \underline{v} . That is, the reactions are of the form



The $\underline{\nu}$ matrix contains the stoichiometric coefficients of only the products, and subscripts for reactions have the same index as those for the corresponding components. Solutes or non-dissociating components are considered to undergo the reaction



so that they appear in the final expressions.

Our equilibrium equations now become

$$\underline{\mu}_O = \underline{\nu}^T \underline{\mu} \quad (2-26a)$$

$$\underline{\bar{M}}_O = \underline{\nu}^T \underline{\bar{M}} \quad (2-26b)$$

and the material balance is written

$$\underline{N} = \underline{\nu} \underline{N}_O \quad (2-27)$$

Now, however, the species vectors do not include any dissociating components, so are of dimension $n - n_O + n_s$, where n_s is the number of components that do not undergo dissociation (solvents = $n_s < n_O$).

In the case of ions and groups, the actual standard states are left to be defined, so we choose $\underline{\mu}^O$ as for equations (2-15)

$$\underline{\mu}_O^O \equiv \underline{\nu}^T \underline{\mu}^O \quad (2-28)$$

with no loss of generality. This leads to a projectable vector of activities,

$$\underline{v}^T \underline{\ln \hat{a}} = \underline{\ln \hat{a}}_0 \quad (2-29a)$$

or

$$\underline{v}^T \underline{\ln \gamma} = \underline{\ln \gamma}_0 + \underline{\ln x}_0 - \underline{v}^T \underline{\ln x} \quad (2-29b)$$

As noted above, the "mean" component set can be chosen equation (2-24) so that for completely dissociated salts equation (2-25) becomes

$$\underline{\ln \gamma}_{\pm} = \frac{\underline{v}^T \underline{\ln \gamma}}{n} \quad (2-30)$$

with mean ionic activity coefficients γ_{\pm} and mean ionic concentrations for x_{\pm} (Harned and Owen, 1958; Robinson and Stokes, 1965).

Application to Analytic Solution of Groups: UNIFAC and UNIQUAC

There are two general situations where group contribution methods are used in correlation of thermodynamic properties. One is when the parameters of a molecular correlation are obtained by summing contributions from the atomic groupings in the molecules. For example, energy and volume parameters have been calculated in various models from sums of group energy and volume contributions (Reid et al., 1977). The method of projection operators as we discuss above does not add anything to these developments because the groups are not considered to have any thermodynamic property values. The projection of parameters does not require the same care as the projection of properties.

The other situation where group contributions are used is in such cases as the "analytical solution of groups" methods (ASOG) (Derr and Deal, 1968, 1969, 1973). Here the groups are considered to have activity coefficients which are summed to obtain molecular activity coefficients. The present analysis leads to significant results because it allows a detailed exploration into the relationships between such theories for groups (species) as UNIFAC and their complementary molecular (component) theories such as UNIQUAC. Projection operators show how it is that the two equations do not yield the same composition dependence for system partial molar properties. As shown below, this difference can yield complete miscibility using UNIFAC but only partial miscibility for UNIQUAC when the two binary parameters for the latter are obtained only from the infinite dilution activity coefficients predicted by UNIFAC.

The UNIQUAC model (Abrams and Prausnitz, 1975; Maurer and Prausnitz, 1978) for mixtures gives an expression for the excess Gibbs free energy of a system of molecules. In the UNIQUAC Functional-group Activity Coefficients model (Fredenslund et al., 1975, 1977a,b; Skjold-Jorgenson, et al., 1979) (UNIFAC), the residual portion of the excess Gibbs free energy is written in terms of the group contributions using the identical expressions for the composition relations, but involving projections of the group parameters.

This expression was chosen by physical arguments after UNIQUAC was developed and the question can be raised about whether equation (C-3b) represents a proper projection of (C-4), which would then lead to identical results for both equations. If not, the activity coefficients can be matched at only one composition other than pure component.

Since it is preferable to project a complete thermodynamic property instead of a portion, we have examined the energies, instead of the free energies, as given in the derivations of the models. This eliminates the combinatorial term which yields the same results for both equations and focuses only on the residual terms where the differences arise.

Figure 4 shows how projections can be applied to solutions of groups. A three dimensional representation is given of the excess enthalpies, H^E , of a solution of hydroxyl, methyl and methylene groups

$$H^E \approx U^E \equiv U - \sum_i x_i \lim_{x_i \rightarrow 1} U \quad (2-31)$$

where equation (C-6) has been used with parameters ΔU_{ki} from Skjold-Jorgensen et al. (1979). Vertical planes representing mixtures of n-pentane with methanol, ethanol or n-pentanol are shown with the projections being the heavy lines in the curved surface. The ideal solution line for these binary mixtures is the straight line in the plane which connects the values of H^E at the two pure component positions. A portion of the methanol-n-pentane line is shown. The desired value for the system, $H_{O_2}^E$, is the vertical distance from the ideal solution line to the H^E surface. As can be seen, the shapes of the $H_{O_2}^E$ curves will vary because curvature of the H^E surface varies with chain length.

While the plot represents an exact projection, the ASOG method also relates the group and molecular properties. In fact, because the same analytic expressions are used, expressions for the partial molar energies, \bar{U}_{on} and \bar{U}_ℓ , look very similar.

EXCESS ENTHALPIES FROM UNIFAC FOR n-ALCOHOL-n-PENTANE SYSTEMS AT 298K

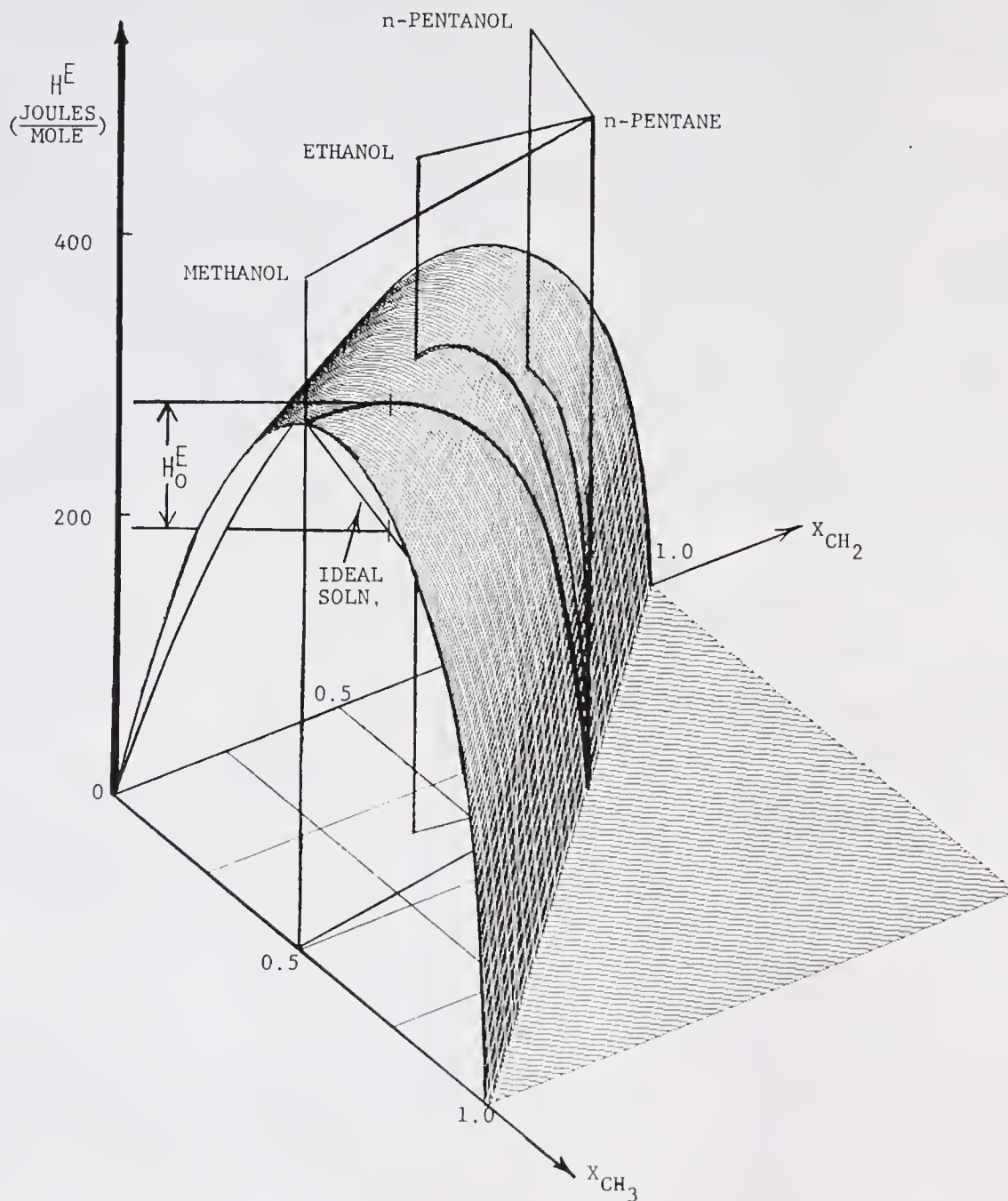


Figure 4. Excess enthalpies from UNIFAC for n-alcohol-n-pentane systems at 298K.

However, the test can be made whether the true projection

$$\bar{U}_{on} \stackrel{?}{=} \sum_{\ell} v_{\ell n} \bar{U}_{\ell} \quad (2-32)$$

exists as required by equation (2-26b). The actual expressions are given in Appendix C. They show that due to the complicated interrelations of the indices in what are otherwise very similar summations, it is clear the molecular energy parameters cannot be related to the group energy parameters in order to make the two expressions become equivalent. This is because the weighted group surface fractions, θ_{ij} , cannot be projected to give a set of weighted molecular surface fractions, $\theta_{\alpha\beta}$, consistent with the projections of the group surface areas, \underline{Q} , to the molecular surface areas \underline{q} , and \underline{N}_0 to \underline{N} . It is possible to achieve numerical equivalence of the energies at any particular solution composition besides unity, but the parameter relationships will vary with concentration. This means that the composition dependence of the component activity coefficients calculated from UNIFAC will be different from those calculated from UNIQUAC even if the values match at any one point, say infinite dilution. Thus, UNIFAC should be considered as different from UNIQUAC as, for example, the Wilson equation is.

If the numerical differences are not large, then the procedure suggested by Fredenslund et al. (1977b) can be used to minimize computation time by finding UNIQUAC component binary parameters from UNIFAC infinite dilution activity coefficients and calculating vapor-liquid equilibrium using UNIQUAC equations.

On the other hand, a particularly significant problem can occur if the difference is large. Since the slope of the binary UNIQUAC activity coefficient is always less than that predicted by UNIFAC at low concentrations, when the infinite dilution values are matched, situations can arise where UNIQUAC predicts liquid-liquid immiscibility even though UNIFAC does not.¹ For instance, this happens in the isopropanol-water system at 1.013 bar (see Figure 5). This problem can be avoided by fitting the UNIFAC infinite dilution values to obtain Wilson equation parameters. In fact, this may be the best procedure in any case for the miscible systems.

¹Multiple solutions for UNIQUAC parameters can be found by this procedure in some systems (Fredenslund, 1980), but we have not found this in the present case.

FREE ENERGIES OF MIXING FOR ISOPROPANOL-WATER AT 1 ATM

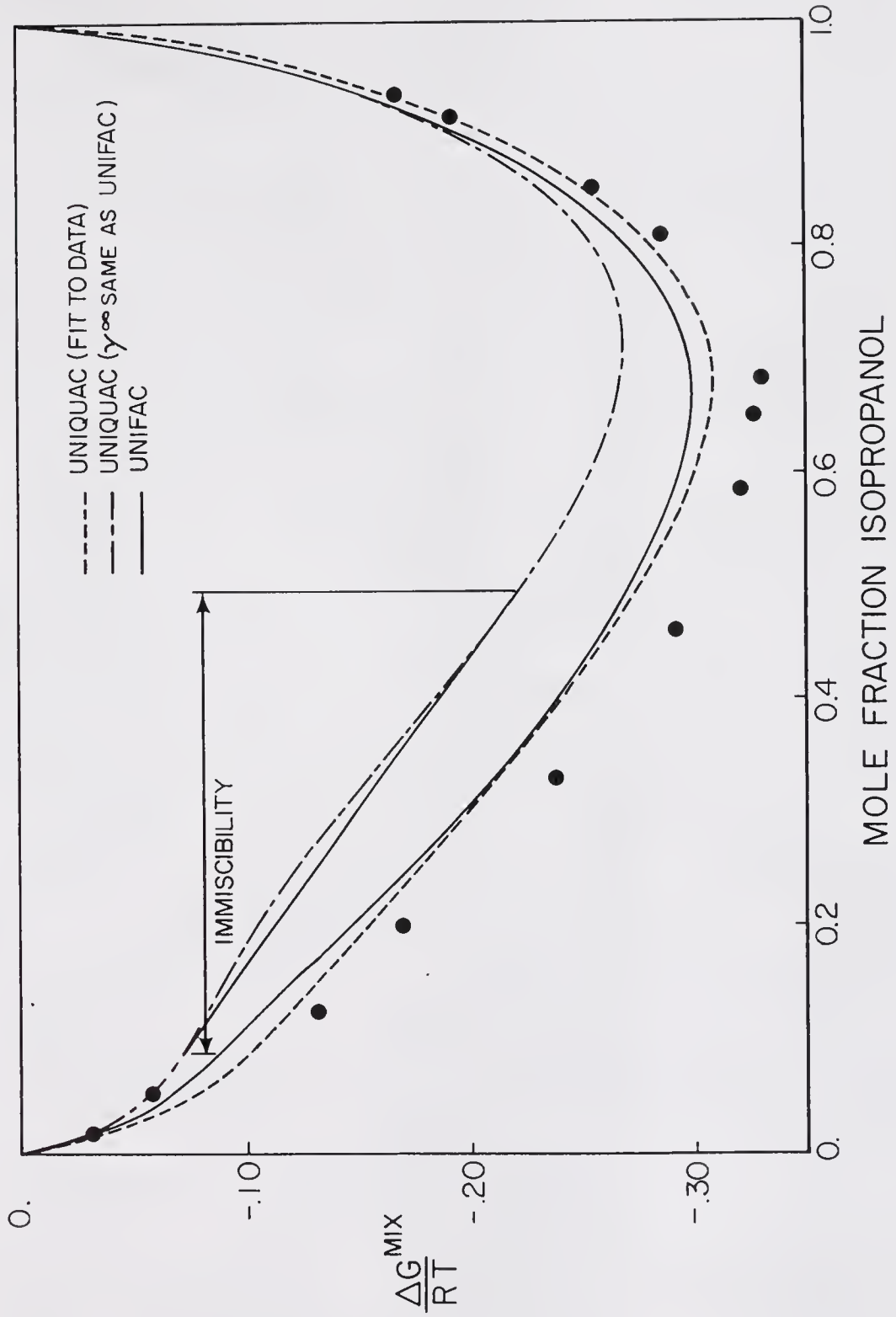


Figure 5. Free energies of mixing for isopropanol(1)-water(2) at 1 atm.

CHAPTER 3
STATISTICAL THERMODYNAMICS OF "REACTIVE"
COMPONENTS IN THE GRAND ENSEMBLE

Introduction

There are two general methods for relating thermodynamic properties of solutions to statistical mechanical correlation functions. One arises from the canonical ensemble, usually assuming pairwise additivity of the intermolecular potentials, which expresses excess energies or free energies in terms of differences of integrals involving the species pair potentials and radial distribution functions (Hill, 1956; Reed and Gubbins, 1973). The other method, from the grand ensemble, relates concentration derivatives of the chemical potential to integrals over the total correlation function (Kirkwood and Buff, 1951; Hall, 1971; O'Connell, 1971) and the direct correlation function (O'Connell, 1971). While modelling studies have been done for both procedures, the latter has recently been shown to be a powerful technique for solutions containing supercritical compounds dissolved in liquids at elevated pressures (Mathias and O'Connell, 1979, 1980a,b). The correlation of electrolyte solution properties (DeGance and O'Connell, 1975) is another application of interest and will be treated in subsequent chapters. Furthermore, the direct correlation functions from the grand ensemble can be used in the formalism of Chapter 2. The purpose of this chapter is to apply the projection formalism in such a way as to establish fundamental statistical mechanical relations in systems with arbitrary reaction schemes.

Components and Species in Complex Systems

We consider the closed system of Chapter 1, constructed from n_0 neutral components that may undergo reactions, dissociations and associations to arrive at an equilibrium system of n chemically identifiable or hypothetical species, neutral or ionic. As before, the material balance which relates the vector of the particle numbers of the species, \underline{N} ,¹ to that of the components, \underline{N}_0 , is

$$\underline{N} = \underline{W} \underline{N}_0 \quad (3-1)$$

where \underline{W} is as defined previously.

In this more detailed analysis, we must use the structure of \underline{W} and related matrices to obtain the desired results. We look here at the case of no successive reactions, and leave the general case to Appendix D. In this simple case, we have, as in Chapter 1,

$$\underline{W} = \underline{L} + \underline{v} \underline{\xi} \quad (3-2)$$

¹ In this chapter, the vector \underline{N} will have two meanings. When used in an obviously macroscopic sense, \underline{N} is the vector of the particle numbers of the species in the system of interest. However, in the statistical mechanical derivations beginning in the next section, \underline{N} will denote the composition vector of a specific system in the ensemble, and $\langle \underline{N} \rangle$ will denote the average of \underline{N} over all the systems of the ensemble, and so corresponds to the \underline{N} used previously. Later, we will return to using \underline{N} instead of $\langle \underline{N} \rangle$, which is cumbersome.

The \underline{L} matrix is of dimension $n \times n_0$, where the first n_0 rows have the form of an $n_0 \times n_0$ identity matrix and the remaining $n-n_0$ rows contain only zeroes. \underline{L} can then be written as

$$\underline{L} = \begin{pmatrix} \underline{I} \\ \underline{0} \end{pmatrix} \quad (3-3)$$

The \underline{v} matrix is of dimension $n \times r$ and can be decomposed in the following manner. We call the first n_0 rows \underline{v}_C ($n_0 \times r$) which contain the stoichiometric coefficients of the components in the reaction scheme. We next note that the reaction equilibria are defined by

$$\underline{v}_\mu^T = 0 \quad (3-4)$$

where $\underline{\mu}$ again is the vector of species chemical potentials. Since the n_0 component chemical potentials are independent and equation (3-4) puts r constraints on $\underline{\mu}$, a given system (fixed $\underline{\mu}_0$) has n_0+r total constraints on $\underline{\mu}$. This leaves $n-n_0-r$ "degrees of freedom" in $\underline{\mu}$.¹ That is, $n-n_0-r$ chemical potentials can be varied independently without changing the values of $\underline{\mu}_0$ and without violating equation (3-4). Of course, the other r chemical potentials will be functions of the chemical potentials which are chosen to be "independent".²

Following these identifications, we now define matrix \underline{v}_D ($r \times r$) which contains the stoichiometric coefficients of the "dependent" species, and the matrix \underline{v}_I which contains the stoichiometric

¹These are not degrees of freedom in a normal sense in that a fixed T, V, μ_0 fixes all of $\underline{\mu}$, but if $\underline{\mu}_0$ is fixed there may be multiple solutions to $\underline{v}_\mu^T = 0$.

²The identification of these species is not unique. There will be some species which cannot be independent in this sense, but in general there are many ways to divide the independent and dependent species.

coefficients of the "independent" species. Because of the manner of construction, \underline{v}_D will be nonsingular, so \underline{v}_D^{-1} will always exist.

Using these identifications, we can rewrite \underline{v} and \underline{W} as

$$\underline{v} = \begin{pmatrix} \underline{v}_C \\ \underline{v}_D \\ \underline{v}_I \end{pmatrix} \quad (3-5)$$

and

$$\underline{W} = \begin{pmatrix} \underline{I} + \underline{v}_C \underline{\xi} \\ \underline{v}_D \underline{\xi} \\ \underline{v}_I \underline{\xi} \end{pmatrix} \quad (3-6)$$

The matrix \underline{W} has dimensions $n \times n_0$ with rank n_0 , provided all the original components appear in the final system.¹ This means that \underline{W} maps \underline{N}_0 onto an n_0 -dimensional "component subspace" in the n -dimensional "species space," and therefore there exists a space of dimension $n-n_0$ in the species space which is orthogonal to the component subspace, and thus to the columns of \underline{W} . We define \underline{Z} as an $n \times (n-n_0)$ matrix made up of a set of vectors which span this space orthogonal to \underline{W} . Then

$$\underline{Z}^T \underline{W} = \underline{0} \text{ and so, } \underline{Z}^T \underline{N} = \underline{0} \quad (3-7)$$

Of course, any set of vectors which span this space can be used to construct \underline{Z} , and in general each element of \underline{Z} is a function of the

¹Another situation arises in the case of completely dissociated electrolytes, for example. Then the rank of \underline{W} can be less than n_0 . The formulation must be slightly modified so that the above analysis is still applicable. The details are given below.

extent of reaction. For convenience, we will construct a specific \underline{Z} consisting of two parts: \underline{Z}_0 , which is $n \times (n-n_0-r)$ and has elements which are independent of the ξ_k 's, and \underline{Z}_1 which is $n \times r$ and has elements which are functions of the ξ_k 's. \underline{Z}_0 can be written explicitly as

$$\underline{Z}_0 = \begin{pmatrix} \underline{0} \\ -(\underline{v}_D^T)^{-1} \underline{v}_I^T \\ \underline{I} \end{pmatrix} \quad (3-8)$$

with $\underline{0}$ being $n_0 \times (n-n_0-r)$ and \underline{I} being $(n-n_0-r) \times (n-n_0-r)$. It is clear that

$$\underline{Z}_0^T \underline{W} = \underline{0}^T (\underline{I} + \underline{v}_C \underline{\xi}) - \underline{v}_I \underline{v}_D^{-1} \underline{v}_D + \underline{I} \underline{v}_I = -\underline{v}_I + \underline{v}_I = \underline{0}$$

as desired.

The \underline{Z}_1 matrix is defined by the following relations:

$$\underline{Z}_1^T \underline{W} = \underline{0} \quad (3-9a)$$

$$\underline{Z}_1^T \underline{Z}_0 = \underline{0} \quad (3-9b)$$

$$\underline{Z}_1^T \underline{Z}_1 = \underline{I} \quad (3-9c)$$

which completely define \underline{Z}_1 . The \underline{Z} matrix can now be written as

$$\underline{Z} = (\underline{Z}_0, \underline{Z}_1) \quad (3-10)$$

which does span the $(n-n_0)$ -dimensional subspace orthogonal to \underline{W} as desired.

We also must construct two $n \times n_o$ matrices, \underline{U} and \underline{Y} , which project in the direction opposite to \underline{W} . First, \underline{U} is important since it spans the same space as \underline{W} , whereas \underline{Y} is important because its elements are independent of the extents of reaction. The defining relations for \underline{U} are

$$\underline{U}^T \underline{W} = \underline{I} \quad (3-11a)$$

$$\underline{U}^T \underline{Z} = \underline{0} \quad (3-11b)$$

and it has the property that

$$\underline{U}^T \underline{N} = \underline{N}_o \quad (3-12)$$

We can write \underline{Y} explicitly as

$$\underline{Y} = \begin{pmatrix} \underline{I} \\ -(\underline{v}_D^T)^{-1} \underline{v}_C \\ \underline{0} \end{pmatrix} \quad (3-13)$$

with \underline{I} being $n_o \times n_o$ and $\underline{0}$ being $(n-n_o-r) \times n_o$. Also

$$\underline{Y}^T \underline{N} = \underline{N}_o \quad (3-14a)$$

but

$$\underline{Y}^T \underline{Z} \neq \underline{0} \quad (3-14b)$$

Grand Ensemble for Systems of "Reactive" Components

To establish the statistical thermodynamic relations among the components and species, we begin by establishing an ensemble with N_T systems, total energy $N_T \langle E \rangle$, and $N_T \langle N_i \rangle$ particles of each species i . The number of ways, t , of having a given distribution of $n_{\underline{N}q}$'s, where $n_{\underline{N}q}$ is the number of systems in quantum state q with particle number vector \underline{N} is

$$t = \frac{N_T!}{\prod_q \prod_{\underline{N}} n_{\underline{N}q}!} \quad (3-15)$$

In Stirling's approximation,

$$\ln t = N_T \ln N_T - N_T - \sum_{\underline{N}} \sum_q (n_{\underline{N}q} \ln n_{\underline{N}q} - n_{\underline{N}q}) \quad (3-16)$$

Using the assumption of equal a priori probabilities, $\ln t$ is maximized to find the most probable distribution, subject to the constraints of constant total size and energy and the overall material balance equations. These constraints, with their Lagrange multipliers, are

$$\sum_{\underline{N}} \sum_q n_{\underline{N}q} = N_T \quad \alpha \quad (3-17a)$$

$$\sum_{\underline{N}} \sum_q n_{\underline{N}q} E_{\underline{N}q} = N_T \langle E \rangle \quad -\beta \quad (3-17b)$$

$$\sum_{\underline{N}} \sum_{\underline{q}} n_{\underline{Nq}} \underline{U}_{\underline{N}}^T = N_{\underline{T}} \underline{U}_{<\underline{N}>}^T = N_{\underline{T-o}} \underline{U}_{\underline{N}}^T \quad \underline{\ell n \lambda} \quad (3-18a)$$

$$\sum_{\underline{N}} \sum_{\underline{q}} n_{\underline{Nq}} \underline{Z}_{\underline{N}}^T = N_{\underline{T}} \underline{Z}_{<\underline{N}>}^T = \underline{0} \quad \underline{\ell n \theta} \quad (3-18b)$$

where $\underline{\ell n \lambda}$ and $\underline{\ell n \theta}$ are vectors of dimension n_o and $n-n_o$ respectively and whose elements are $\ell n \lambda_{\alpha}$ and $\ell n \theta_k$. The equation for the maximum in $\ell n t$ is

$$\begin{aligned} d(\ell n t) + \alpha \sum_{\underline{N}} \sum_{\underline{q}} d n_{\underline{Nq}} - \beta \sum_{\underline{N}} \sum_{\underline{q}} E_{\underline{Nq}} d n_{\underline{Nq}} + (\underline{\ell n \lambda})^T \sum_{\underline{N}} \sum_{\underline{q}} \underline{U}_{\underline{N}}^T d n_{\underline{Nq}} \\ + (\underline{\ell n \theta})^T \sum_{\underline{N}} \sum_{\underline{q}} \underline{Z}_{\underline{N}}^T d n_{\underline{Nq}} = 0 \end{aligned} \quad (3-19)$$

Equation (3-16) gives, upon differentiation

$$d(\ell n t) = - \sum_{\underline{N}} \sum_{\underline{q}} \ell n n_{\underline{Nq}} d n_{\underline{Nq}}$$

which with equation (17) leads to

$$-\ell n n_{\underline{Nq}} + \alpha - \beta E_{\underline{Nq}} + (\underline{\ell n \lambda})^T \underline{U}_{\underline{N}}^T + (\underline{\ell n \theta})^T \underline{Z}_{\underline{N}}^T = 0 \quad (3-20)$$

since in the method of Lagrange multipliers the $n_{\underline{Nq}}$ are treated as independent.

Solving equation (3-20) for $n_{\underline{Nq}}$, we have, for all values of \underline{N} and \underline{q}

$$n_{\underline{Nq}} = \exp \{ \alpha - \beta E_{\underline{Nq}} + (\underline{\ell n \lambda})^T \underline{U}_{\underline{N}}^T + (\underline{\ell n \theta})^T \underline{Z}_{\underline{N}}^T \} \quad (3-21)$$

Defining

$$\Xi(\underline{\lambda}, \underline{\theta}, \beta, V) = \sum_{\underline{N}} \sum_q \exp \{-\beta E_{\underline{N}q} + (\underline{\lambda n \lambda})^T \underline{U}^T \underline{N} + (\underline{\lambda n \theta})^T \underline{Z}^T \underline{N}\} \quad (3-22)$$

the probability of finding a system with particle number vector \underline{N} in state q is written as

$$P_{\underline{N}q} = \frac{n_{\underline{N}q}}{T} = \frac{\exp \{-\beta E_{\underline{N}q} + (\underline{\lambda n \lambda})^T \underline{U}^T + (\underline{\lambda n \theta})^T \underline{Z}^T \underline{N}\}}{\Xi(\underline{\lambda}, \underline{\theta}, \beta, V)} \quad (3-23)$$

In the usual case of nonreacting components, the partition function would be written

$$\Xi(\underline{\mu}, \beta, V) = \sum_{\underline{N}} \sum_q \exp \{-\beta E_{\underline{N}q} + \beta \underline{\mu}^T \underline{N}\} \quad (3-24)$$

where \underline{N} is the same vector as in equation (3-22), β is $1/k_B T$ and $\underline{\mu}$ is the vector of species chemical potentials. By comparing equations (3-22) and (3-24) we should expect that $\underline{\lambda n \lambda}$ and $\underline{\lambda n \theta}$ can be identified by the relation

$$\beta \underline{\mu} = \underline{U} \underline{\lambda n \lambda} + \underline{Z} \underline{\lambda n \theta} \quad (3-25)$$

This identification, if correct, has several interesting results. Using equation (2-5) and equations (3-11)

$$\beta \underline{\mu}_O = \beta \underline{W}^T \underline{\mu} = \underline{\lambda n \lambda} \quad (3-26)$$

Furthermore, equations (2-2), (2-3) and the Gibbs-Duhem equation lead to, after some manipulation and use of equations (3-11)

$$\{(\underline{\ln\lambda})^T d\underline{U} + (\underline{\ln\theta})^T d\underline{Z}\} <\underline{N}> = \underline{0} \quad (3-27)$$

provided the differentials are taken along an equilibrium path.

Equation (3-26) identifies $\beta^{-1} \underline{\ln\lambda}$ with the chemical potentials of the components. Equation (3-27) will be useful in later manipulations.

The identification in equation (3-25) is only a proposition, and it must be shown to be a solution. We will assume it is a solution and then test the validity of this assumption. We begin by examining the average entropy for a system in the grand ensemble,

$$<S> = -k_B \sum_{\underline{N}} \sum_q p_{\underline{N}q} \ln p_{\underline{N}q}$$

or, substituting equation (3-23) for $p_{\underline{N}q}$ in this relation

$$<S>/k_B = \beta <E> - (\underline{\ln\lambda})^T \underline{N}_O + \ln \Xi \quad (3-28)$$

For the Helmholtz free energy, A, we have

$$\beta A = \beta <E> - <S>/k_B = (\underline{\ln\lambda})^T \underline{N}_O + \ln \Xi \quad (3-29)$$

The chemical potential of component α in component space is

$$\beta \mu_{\alpha} = \beta \frac{\partial A}{\partial N_{\alpha}} \bigg|_{T, V, N_{\gamma \neq \alpha}} = \frac{\partial (\underline{\ln\lambda})^T}{\partial N_{\alpha}} \bigg|_{T, V, N_{\gamma \neq \alpha}} \underline{N}_O + \ln \lambda_{\alpha} - \frac{\partial \ln \Xi}{\partial N_{\alpha}} \bigg|_{T, V, N_{\gamma \neq \alpha}} \quad (3-30)$$

where it is important to note that it is the amounts of the other components ($N_{O\gamma}$) as initially charged to the system before reaction occurs, and not the amounts of the species, that are held constant. We assume that a change in a component concentration is done with all reactions at equilibrium. Thus the species concentrations are known from the component values, $N_{O\alpha}$, and the material balance based on equilibrium extents of reaction (\underline{W}). With these restrictions all the derivatives in equation (3-30) are taken along an equilibrium path, making equation (3-27) applicable.

Since $\underline{\ln\lambda}$ and $\underline{\ln\theta}$ are functions of $N_{O\alpha}$, equation (3-30) can be written

$$\begin{aligned} \beta_{\mu_{O\alpha}} = & \frac{\partial(\underline{\ln\lambda})^T}{\partial N_{O\alpha}} \bigg|_{T, V, N_{O\gamma \neq \alpha}} \underline{N}_{O\alpha} + \underline{\ln\lambda}_{O\alpha} - \frac{\partial(\underline{\ln\lambda})^T}{\partial N_{O\alpha}} \bigg|_{T, V, N_{O\gamma \neq \alpha}} \underline{U}_{<\underline{N}>}^T - (\underline{\ln\lambda})^T \frac{\partial \underline{U}^T}{\partial N_{O\alpha}} \bigg|_{T, V, N_{O\gamma \neq \alpha}} <\underline{N}> \\ & - \frac{\partial(\underline{\ln\theta})^T}{\partial N_{O\alpha}} \bigg|_{T, V, N_{O\gamma \neq \alpha}} \underline{Z}_{<\underline{N}>}^T - (\underline{\ln\lambda})^T \frac{\partial \underline{Z}^T}{\partial N_{O\alpha}} \bigg|_{T, V, N_{O\gamma \neq \alpha}} <\underline{N}> \end{aligned} \quad (3-31)$$

The first and third terms on the right hand side of equation (3-31) cancel by equation (3-12), the fourth and sixth are zero by equation (3-27) and the fifth term is zero by equation (3-7). This leaves us with the desired result

$$\beta_{\mu_{O\alpha}} = \underline{\ln\lambda}_{O\alpha}$$

or

$$\beta_{\underline{O}} = \underline{\ln\lambda} \quad (3-32)$$

as proposed in equation (3-25) and (3-26). Thus we find that these equations are indeed a solution for the Lagrange multipliers $\underline{\ln\lambda}$ and $\underline{\ln\theta}$.

Equation (3-32) not only defines the Lagrange multiplier $\ln\lambda_\alpha$ but also shows us what the independent variables for the grand canonical ensemble are. We already know that a macroscopic (canonical) system can be determined by fixing T, V and \underline{N}_0 , a total of n_0+2 variables. Similarly, in the grand ensemble, we fix the same number of variables T, V and $\underline{\mu}_0$ (or $\underline{\ln\lambda}$) to completely determine the thermodynamic state. This fact is very important in taking derivatives of ensemble averages, since this means there is a relationship between the elements of $\underline{\ln\theta}$ and the elements of $\underline{\ln\lambda}$. This dependence and important thermodynamic derivatives of the ensemble are given in Appendix E.

Composition Fluctuations

Macroscopic thermodynamic properties of the ensemble can be related to microscopic properties through the density fluctuations in the systems of the ensemble. We define the fluctuation matrix, \underline{A} , by

$$\underline{A} = \frac{1}{\langle \underline{N} \rangle} (\langle \underline{NN}^T \rangle - \langle \underline{N} \rangle \langle \underline{N}^T \rangle) \quad (3-33)$$

with
$$\langle \underline{N} \rangle = \frac{1}{\Xi} \sum_{\underline{N}} \sum_{\underline{q}} \underline{N} \exp \{ -\beta E_{\underline{Nq}} + \underline{N}^T (\underline{U} \underline{\ln \lambda} + \underline{Z} \underline{\ln \theta}) \} \quad (3-34a)$$

$$\langle \underline{N} \rangle = \sum_{\underline{i}} \langle N_{\underline{i}} \rangle \quad (3-34b)$$

$$\langle \underline{NN}^T \rangle = \frac{1}{\Xi} \sum_{\underline{N}} \sum_{\underline{q}} \underline{NN}^T \exp \{ -\beta E_{\underline{Nq}} + \underline{N}^T (\underline{U} \underline{\ln \lambda} + \underline{Z} \underline{\ln \theta}) \} \quad (3-34c)$$

Equation (3-34a) can be differentiated with respect to a component chemical potential along the equilibrium path to obtain the relationship between the fluctuations and macroscopic properties (details are given in Appendix E). This differentiation leads to

$$\begin{aligned} \left. \frac{1}{\langle \underline{N} \rangle} \frac{\partial \langle \underline{N} \rangle}{\partial \beta \mu_{o\alpha}} \right|_{T, V, \mu_{o\gamma \neq \alpha}} &= \frac{1}{\langle \underline{N} \rangle} \langle \underline{NN}^T \rangle \left[\left(\underline{Y} \right)_{\alpha} + \underline{Z} \frac{\partial \mu_{\underline{I}}}{\partial \beta \mu_{o\alpha}} \right]_{T, V, \mu_{o\gamma \neq \alpha}} \\ &- \frac{1}{\langle \underline{N} \rangle} \langle \underline{N} \rangle \langle \underline{N}^T \rangle \left(\underline{Y} \right)_{\alpha} \end{aligned} \quad (3-35a)$$

$$= \underline{A} \left[\left(\underline{Y} \right)_{\alpha} + \underline{Z}_o \frac{\partial \underline{\mu}_I}{\partial \underline{\mu}_{o\alpha}} \right]_{T, V, \mu_{o\gamma \neq \alpha}} \quad (3-35b)$$

where the notation $(\underline{Y})_{\alpha}$ denotes the α -th column of \underline{Y} .

We can use equation (3-14a) to project the left hand side of this equation into component space. Defining the matrix \underline{A}

$$\begin{aligned} (\underline{A})_{\alpha\beta} &= (\underline{A})_{\beta\alpha} \equiv \frac{1}{\langle N \rangle} \frac{\partial N_{o\beta}}{\partial \beta \mu_{o\alpha}} \bigg|_{T, V, \mu_{o\gamma \neq \alpha}} = \frac{1}{\langle N \rangle} (\underline{Y})_{\beta}^T \frac{\partial \langle N \rangle}{\partial \beta \mu_{o\alpha}} \bigg|_{T, V, \mu_{o\gamma \neq \alpha}} \\ &= \frac{1}{\langle N \rangle} (\underline{Y})_{\beta}^T \langle \underline{N} \underline{N}^T \rangle \left[\left(\underline{Y} \right)_{\alpha} + \underline{Z}_o \frac{\partial \underline{\mu}_I}{\partial \underline{\mu}_{o\alpha}} \right]_{T, V, \mu_{o\gamma \neq \alpha}} \\ &\quad - \frac{1}{\langle N \rangle} (\underline{Y})_{\beta}^T \langle \underline{N} \rangle \langle \underline{N}^T \rangle (\underline{Y})_{\alpha} \end{aligned} \quad (3-36)$$

Using equation (3-7) we can rewrite \underline{A} as a projection of \underline{A} ,

$$\begin{aligned} (\underline{A})_{\alpha\beta} &= (\underline{Y})_{\beta}^T \underline{A} \left[\left(\underline{Y} \right)_{\alpha} + \underline{Z}_o \frac{\partial \underline{\mu}_I}{\partial \underline{\mu}_{o\alpha}} \right]_{T, V, \mu_{o\gamma \neq \alpha}} \\ &= \left[(\underline{Y})_{\beta}^T + \frac{\partial \underline{\mu}_I^T}{\partial \underline{\mu}_{o\beta}} \bigg|_{T, V, \mu_{o\gamma \neq \alpha}} \underline{Z}_o^T \right] \underline{A} (\underline{Y})_{\alpha} \end{aligned} \quad (3-37)$$

The next section shows how the \underline{A} matrix is related to the microscopic properties of the species, thus forming a bridge between them and the macroscopic component properties.

Correlation Function Integrals

The method of Kirkwood and Buff (1951) can be used to relate the fluctuation properties of integrals of the radial distribution function and direct correlation function. We define spacially and orientationally dependent one and two particle densities by

$$f_i^{(1)}(\underline{r}_1; \underline{\omega}_1) = \sum_{p=1}^{N_j} (\underline{r}_p - \underline{r}_1) \delta(\underline{\omega}_p - \underline{\omega}_1) \quad i, = 1, \dots, n \quad (3-38a)$$

$$f_{ij}^{(2)}(\underline{r}_1, \underline{r}_2; \underline{\omega}_1, \underline{\omega}_2) = \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \delta(\underline{r}_p - \underline{r}_1) \delta(\underline{r}_q - \underline{r}_2) \delta(\underline{\omega}_p - \underline{\omega}_1) \times \delta(\underline{\omega}_q - \underline{\omega}_2) \quad (3-38b)$$

(p ≠ q if i=j)

where $\delta(\underline{r} - \underline{r}_1)$ is the three dimensional Dirac delta function, \underline{r} is the position vector and $\underline{\omega}$ is the vector of Euler angles of molecular orientation.

By definition, we have

$$\int_{\Omega} \int_V f_i^{(1)}(\underline{r}_1; \underline{\omega}_1) d\underline{r}_1 d\underline{\omega}_1 = N_i \quad (3-39a)$$

$$\int_{\Omega} \int_{\Omega} \int_V \int_V f_{ij}^{(2)}(\underline{r}_1, \underline{r}_2; \underline{\omega}_1, \underline{\omega}_2) d\underline{r}_1 d\underline{r}_2 d\underline{\omega}_1 d\underline{\omega}_2 = N_i N_j - N_i \delta_{ij} \quad (3-39b)$$

We now define ensemble average number densities by

$$\rho_i^{(1)}(\underline{r}_1; \underline{\omega}_1) \equiv \langle f_i^{(1)}(\underline{r}_1; \underline{\omega}_1) \rangle \quad (3-40a)$$

$$\rho_{ij}^{(2)}(\underline{r}_1, \underline{r}_2; \omega_1, \omega_2) \equiv \langle f_{ij}^{(2)}(\underline{r}_1, \underline{r}_2; \omega_1, \omega_2) \rangle \quad (3-40b)$$

Equations (3-39) are integrated to obtain

$$\int_{\Omega} \int_V \rho_i^{(1)}(\underline{r}_1; \omega_1) d\underline{r}_1 d\omega_1 = \langle N_i \rangle \quad (3-41a)$$

$$\int_{\Omega} \int_{\Omega} \int_V \int_V \rho_{ij}^{(2)}(\underline{r}_1, \underline{r}_2; \omega_1, \omega_2) d\underline{r}_1 d\underline{r}_2 d\omega_1 d\omega_2 = \langle N_i N_j \rangle - \langle N_i \rangle \delta_{ij} \quad (3-41b)$$

For fluid systems, we define the mean density and the pair correlation function by

$$\rho_i \equiv \Omega \rho_i^{(1)}(\underline{r}_1; \omega_1) = \langle N_i \rangle / V \quad (3-42)$$

and

$$\rho_i \rho_j g_{ij}(\underline{r}_{12}; \omega_1, \omega_2) \equiv \Omega^2 \rho_{ij}^{(2)}(\underline{r}_1, \underline{r}_2; \omega_1, \omega_2) \quad (3-43)$$

where $\Omega \equiv \int d\omega$.

The pair correlation function can be integrated over its arguments and related to the concentration fluctuations using equation (3-39b), as

$$\langle N_i N_j \rangle - \langle N_i \rangle \delta_{ij} = \frac{\rho_i \rho_j}{\Omega^2} V \int_{\Omega} \int_{\Omega} \int_V g_{ij}(\underline{r}_{12}; \omega_1, \omega_2) d\underline{r}_{12} d\omega_1 d\omega_2 \quad (3-44a)$$

or

$$\langle N_i N_j \rangle - \langle N_i \rangle \delta_{ij} = \rho_i \rho_j V \int_V \langle g_{ij}(\underline{r}_{12}; \omega_1, \omega_2) \rangle_{\Omega_1, \Omega_2} d\underline{r}_{12} \quad (3-44)$$

The angle-averaged (or "centers") total correlation function, $h_{ij}(\underline{r}_{12})$, is defined by

$$h_{ij}(\underline{r}_{12}) = \langle g_{ij}(\underline{r}_{12}; \omega_1, \omega_2) \rangle_{\Omega_1, \Omega_2}^{-1} \quad (3-45)$$

Then using matrix notation

$$(\underline{H})_{ij} \equiv \frac{\langle N \rangle}{V} \int_V h_{ij}(\underline{r}_{12}) d\underline{r}_{12} = \langle N \rangle \left(\frac{\langle N_i N_j \rangle - \langle N_i \rangle \langle N_j \rangle}{\langle N_i \rangle \langle N_j \rangle} - \frac{\delta_{ij}}{\langle N_i \rangle} \right) \quad (3-46)$$

we find

$$\frac{\langle N_i \rangle \langle N_j \rangle}{\langle N^2 \rangle} (\underline{H})_{ij} = \frac{\langle N_i N_j \rangle - \langle N_i \rangle \langle N_j \rangle}{\langle N \rangle} - \frac{\langle N_i \rangle}{\langle N \rangle} \delta_{ij} \quad (3-47)$$

letting $x_i = \langle N_i \rangle / \langle N \rangle$, equations (3-33) and (3-47) yield

$$(\underline{A})_{ij} = x_i \delta_{ij} + x_i x_j (\underline{H})_{ij}$$

or, defining a matrix $(\underline{X})_{ij} = x_i \delta_{ij}$

$$\underline{A} = \underline{X}(\underline{I} + \underline{H} \underline{X}) \quad (3-48)$$

A "centers" direct correlation function can be defined by the equation

$$c_{ij}(\underline{r}_{12}) \equiv h_{ij}(\underline{r}_{12}) - \sum_{\ell=1}^n \int_V c_{\ell j}(\underline{r}_{13}) \rho_{\ell} h_{i\ell}(\underline{r}_{23}) d\underline{r}_3 \quad (3-49)$$

Integrating over \underline{r}_{12} and multiplying by $\langle N \rangle / V$ we find

$$\begin{aligned} \frac{\langle N \rangle}{V} \int_V h_{ij} d\underline{r}_{12} &= \frac{\langle N \rangle}{V} \int_V c_{ij} d\underline{r}_{12} + \frac{\langle N \rangle}{V} \sum_{\ell=1}^n \int_V \int_V c_{\ell j}(\underline{r}_{13}) \rho_{\ell} h_{i\ell}(\underline{r}_{23}) \\ &\quad \times d\underline{r}_3 d\underline{r}_{12} \end{aligned} \quad (3-50)$$

For systems where the matrices \underline{A} , \underline{H} and \underline{C} are all bounded and non-singular¹, Fourier transform theory (Pearson and Rushbrooke, 1957) can be used to obtain

$$\underline{H} = \underline{C} + \underline{H} \underline{X} \underline{C} = (\underline{I} + \underline{H} \underline{X}) \underline{C} \quad (3-51)$$

where

$$(\underline{C})_{ij} = \frac{\langle N \rangle}{V} \int_V c_{ij}(\underline{r}_{12}) d\underline{r}_{12}$$

Some manipulation of equations (3-48) and (3-51) leads to the relationship between \underline{C} and \underline{A} ,

¹Here it has tacitly been assumed that the integral of $c_{ij}(\underline{r}; \rho)$ is not divergent. This is not the case for certain systems, such as those with coulombic interactions. In such a case, the derivation of Chapter 4 must be used.

$$\underline{A}(\underline{X}^{-1} - \underline{C}) = \underline{I} \quad (3-52)$$

Since we have only the components as degrees of freedom, we want to project this into component space. Following equation (3-37) we pre-multiply by

$$(\underline{Y})_{\alpha}^T + \left. \frac{\partial \underline{I}^T}{\partial \mu_{o\alpha}} \right|_{T,V,\mu_{o\gamma \neq \alpha}} \underline{Z}_o^T$$

and post-multiply by \underline{W} , giving

$$\begin{aligned} \left[(\underline{Y})_{\alpha}^T + \left. \frac{\partial \underline{I}^T}{\partial \mu_{o\alpha}} \right|_{T,V,\mu_{o\gamma \neq \alpha}} \underline{Z}_o^T \right] \underline{A}(\underline{X}^{-1} - \underline{C})\underline{W} &= (\underline{Y})_{\alpha}^T \underline{W} \\ &+ \left. \frac{\partial \underline{I}^T}{\partial \mu_{o\alpha}} \right|_{T,V,\mu_{o\gamma \neq \alpha}} \underline{Z}_o^T \underline{W} \end{aligned} \quad (3-53a)$$

or

$$\left. \frac{\partial \langle \underline{N}^T \rangle}{\partial \beta \mu_{o\alpha}} \right|_{T,V,\mu_{o\gamma \neq \alpha}} (\underline{X}^{-1} - \underline{C})\underline{W} = \underline{e}_{\alpha} \quad (3-53b)$$

where \underline{e}_{α} is a vector such that $(\underline{e}_{\alpha})_{\beta} = \delta_{\alpha\beta}$. Differentiation of equation (3-1) leads to

$$\left. \frac{\partial \langle \underline{N}^T \rangle}{\partial \beta \mu_{o\alpha}} \right|_{T,V,\mu_{o\gamma \neq \alpha}} = \left. \frac{\partial \underline{N}_o^T}{\partial \beta \mu_{o\alpha}} \right|_{T,V,\mu_{o\gamma \neq \alpha}} \underline{W}^T + \underline{N}_o^T \left. \frac{\partial \underline{W}^T}{\partial \beta \mu_{o\alpha}} \right|_{T,V,\mu_{o\gamma \neq \alpha}} \quad (3-54)$$

We define the matrix $\underline{K}_{-\mu}$ such that

$$(\underline{K}_{-\mu})_{i\alpha} = \sum_{\gamma=1}^{n_o} N_{o\gamma} \left. \frac{\partial (\underline{W})_{i\gamma}}{\partial \beta_{\mu o\alpha}} \right|_{T, V, \mu_{o\gamma} \neq \alpha} \quad (3-55)$$

Then we can write the general expression in component space by combining equations (3-37), (3-53b), (3-54) and (3-55)

$$\underline{\underline{A}} \underline{\underline{W}}^T (\underline{X}^{-1} - \underline{C}) \underline{\underline{W}} + \underline{K}_{-\mu}^T (\underline{X}^{-1} - \underline{C}) \underline{\underline{W}} = \underline{I} \quad (3-56)$$

where \underline{I} is the $n_o \times n_o$ identity matrix. Multiplying through by \underline{A}^{-1} , we have the desired result

$$\underline{A}^{-1} = (\underline{W} + \underline{K})^T (\underline{X}^{-1} - \underline{C}) \underline{W} \quad (3-57)$$

where

$$\begin{aligned} (\underline{K})_{i\alpha} &= \sum_{\gamma=1}^{n_o} N_{o\gamma} \left. \frac{\partial (\underline{W})_{i\gamma}}{\partial N_{o\alpha}} \right|_{T, V, N_{o\gamma} \neq \alpha} \\ &= \sum_{\gamma=1}^{n_o} N_{o\gamma} \sum_{\beta=1}^{n_o} \beta \left. \frac{\partial \mu_{o\beta}}{\partial N_{o\alpha}} \right|_{T, V, N_{o\gamma} \neq \alpha} \left. \frac{\partial (\underline{W})_{i\gamma}}{\partial \beta_{\mu o\beta}} \right|_{T, V, \mu_{o\gamma} \neq \beta} \\ &= \sum_{\beta=1}^{n_o} (\underline{A}^{-1})_{\alpha\beta} (\underline{K}_{-\mu})_{i\beta} = (\underline{A}^{-1} \underline{K}_{-\mu}^T)_{\alpha i} \end{aligned} \quad (3-58)$$

Equation (3-57), therefore, relates the derivatives of the component chemical potentials in component space to the species direct correlation

functions and the component composition derivatives of the extents of reactions (through \underline{W}).

Because of its complexity, it is not apparent that a single optimal procedure exists for obtaining changes in chemical potentials (and also pressure) by integrating equation (3-57). However, in the case of totally dissociating systems this is straightforward.

Complete Reactions

One kind of system of particular interest is that which, for each reaction, there is a limiting reactant which appears only in that reaction and whose concentration goes to zero in the solution.¹ In such a case, the species composition vector and the extents of reaction can be uniquely determined from \underline{v} and \underline{N}_0 using only algebraic relations (no equilibrium calculations). Examples of this kind of system include solutions of strong electrolytes and "solutions of groups."

Here we make a different partitioning of the matrices of interest. The components are divided into two groups: the limiting reactants which are subscripted L, and the other components which are subscripted S (solvents). The species which are not found as initial components form only one group, which is subscripted P (products). The \underline{W} matrix is then

$$\underline{W} = \begin{pmatrix} \underline{I} & \underline{0} \\ \underline{0} & \underline{I} \\ \underline{0} & \underline{0} \end{pmatrix} + \begin{pmatrix} \underline{v}_S \\ \underline{v}_L \\ \underline{v}_P \end{pmatrix} \quad (\underline{\xi}_S \quad \underline{\xi}_L) \quad (3-59)$$

Since a system of only complete reactions with the above restrictions must have the same number of reactions as it does limiting reactants, we will number each reaction by its corresponding limiting reactant. If n_s is the number of solvents, the partitions of the \underline{W} matrix have the following dimensions:

¹ In the case of where two components of a reaction would go to zero concentration, one is chosen as the limiting reactant and the other treated as an ordinary component. This situation could only occur if these two components had initial compositions with the proper stoichiometric ratio. In the derivation given, only non-sequential reaction schemes are considered. This is general because any sequence of complete reactions can be written as a non-sequential scheme.

\underline{v}_S is $n_S \times (n_O - n_S)$

\underline{v}_L is $(n_O - n_S) \times (n_O - n_S)$

\underline{v}_P is $(n - n_O) \times (n_O - n_S)$

$\underline{\xi}_S$ is $(n_O - n_S) \times n_S$

$\underline{\xi}_L$ is $(n_O - n_S) \times (n_O - n_S)$

To see the simplifications that result in the case of complete reactions, equation (3-57) can be written

$$\underline{A}^{-1} = (\underline{W} + \underline{K}^T)(\underline{X}^{-1} - \underline{C})(\underline{W} + \underline{K}) \quad (3-60)$$

This equation may be obtained from equation (3-52) by following a process identical to equations (3-53) through (3-58) plus postmultiplying equation (3-52) by \underline{K} to obtain

$$\underline{A}(\underline{W} + \underline{K}^T)(\underline{X}^{-1} - \underline{C})\underline{K} = \underline{Y}^T \underline{K} + \left. \frac{\partial \underline{\mu}_I}{\partial \underline{\mu}_{O\alpha}} \right|_{T,V} \underline{Z}_O^T \underline{K} = 0 \quad (3-61)$$

The second equality comes from

$$\underline{Y}^T \underline{K} = \underline{0} \quad \text{and} \quad \underline{Z}_O^T \underline{K} = \underline{0}$$

and $\left. \frac{\partial \underline{\mu}_I}{\partial \underline{\mu}_O} \right|_{T,V}$ is the Jacobian matrix of the derivatives $\left. \frac{\partial (\underline{\mu}_I)_i}{\partial \underline{\mu}_{O\alpha}} \right|_{T,V,\mu_{O\gamma \neq \alpha}}$

Thus,

$$(\underline{W} + \underline{K})^T (\underline{X}^{-1} - \underline{C}) \underline{K} = \underline{0} \quad (3-62)$$

Addition of equations (3-58) and (3-62) gives equation (3-60) as desired.

The projection matrix $\underline{W} + \underline{K}$ is a very sparse matrix compared to either \underline{W} or \underline{K} .

For a complete reaction, written

$$\sum_{i=1}^n B_i v_{i\alpha} = 0$$

with component α being the limiting reactant, we know that

$$N_{\alpha} = 0 = N_{o\alpha} + v_{\alpha\alpha} \xi_{\alpha} N_{or_{\alpha}} \quad (3-63a)$$

where r_{α} is the reference component for reaction α . In the limit of complete reaction, the extent of reaction can be written

$$\xi_{\alpha} = - \frac{1}{v_{\alpha\alpha}} \frac{N_{o\alpha}}{N_{or_{\alpha}}} \quad (3-63b)$$

The general term in the \underline{W} matrix is

$$(\underline{W})_{i\beta} = \delta_{i\beta} + \sum_{\alpha=n_s+1}^{n_o} v_{i\alpha} \left(-\frac{1}{v_{\alpha\alpha}} \frac{N_{o\alpha}}{N_{or_{\alpha}}} \right) \delta_{\beta r_{\alpha}} \quad (3-64)$$

Similarly, for the \underline{K} matrix

$$\begin{aligned} (\underline{K})_{i\beta} &= \sum_{\gamma=1}^{n_o} N_{o\gamma} \sum_{\alpha=n_s+1}^{n_o} \left(-\frac{v_{i\alpha}}{v_{\alpha\alpha}} \right) \delta_{\gamma r_{\alpha}} \frac{\delta_{\alpha\beta} N_{or_{\alpha}} - N_{o\alpha} \delta_{\beta r_{\alpha}}}{N_{or_{\alpha}}^2} \\ &= - \sum_{\alpha=n_s+1}^{n_o} \frac{v_{i\alpha}}{v_{\alpha\alpha}} \delta_{\alpha\beta} + \sum_{\alpha=n_s+1}^{n_o} \frac{v_{i\alpha}}{v_{\alpha\alpha}} \frac{N_{o\alpha}}{N_{or_{\alpha}}} \delta_{\beta r_{\alpha}} \end{aligned} \quad (3-65)$$

Addition of equations (3-64) and (3-65) yields the general element of the projection matrix

$$(\underline{W+K})_{i\beta} = \delta_{i\beta} - \sum_{\alpha=n_s+1}^{n_o} \frac{v_{i\alpha}}{v_{\alpha\alpha}} \delta_{\alpha\beta} \quad (3-66)$$

If index β is between 1 and n_s (solvent), we have simply

$$(\underline{W+K})_{i\beta} = \delta_{i\beta} \quad 1 \leq \beta \leq n_s; 1 \leq \alpha \leq n \quad (3-67)$$

which defines the first n_s columns of $(\underline{W+K})$. If β is between n_s+1 and n_o (limiting reactant) we have three possibilities: For i being a solvent ($1 \leq i \leq n_s$),

$$(\underline{W+K})_{i\beta} = -\frac{v_{i\beta}}{v_{\beta\beta}} \quad 1 \leq i \leq n_s; n_s+1 \leq \beta \leq n. \quad (3-68a)$$

For i being a limiting reactant ($n_s+1 \leq i \leq n_o$)

$$(\underline{W+K})_{i\beta} = 0 \quad n_s+1 \leq i, \beta \leq n_o \quad i \neq \beta \quad (3-68b)$$

$$(\underline{W+K})_{i\beta} = 1 - \frac{v_{\beta\beta}}{v_{\beta\beta}} = 0 \quad n_s+1 \leq i, \beta \leq n_o \quad i = \beta \quad (3-68c)$$

Finally, for i being a product ($n_o+1 \leq i \leq n$)

$$(\underline{W+K})_{i\beta} = -\frac{v_{i\beta}}{v_{\beta\beta}} \quad n_o+1 \leq i \leq n; n_s+1 \leq \beta \leq n_o \quad (3-69)$$

Since \underline{v}_L (made up solely of the $v_{\beta\beta}$'s) is diagonal, equations (3-65) and (3-69) can be written in matrix form.

$$\underline{W+K} = \begin{pmatrix} \underline{I} & -\underline{v}_S \underline{v}_L^{-1} \\ \underline{0} & \underline{0} \\ \underline{0} & -\underline{v}_P \underline{v}_L^{-1} \end{pmatrix} \quad (3-70)$$

Partitioning $(\underline{X}^{-1}-\underline{C})$ in a similar manner yields

$$\underline{X}^{-1}-\underline{C} = \begin{pmatrix} \underline{X}_S^{-1}-\underline{C}_{SS} & -\underline{C}_{LS}^T & -\underline{C}_{PS}^T \\ -\underline{C}_{LS} & -\underline{C}_{LL} & -\underline{C}_{PL}^T \\ -\underline{C}_{PS} & -\underline{C}_{PL} & \underline{X}_P^{-1}-\underline{C}_{PP} \end{pmatrix} + \begin{pmatrix} \underline{0} & \underline{0} & \underline{0} \\ \underline{0} & \underline{X}_L^{-1} & \underline{0} \\ \underline{0} & \underline{0} & \underline{0} \end{pmatrix} \quad (3-71)$$

The first matrix on the right hand side is well-behaved in the limit of complete reactions. However, the second matrix diverges and must be operated on by $(\underline{W}+\underline{K})$ before the limit of complete reactions is taken. This procedure is carried out in Appendix F and leads to the equation

$$\lim_{\substack{\text{complete} \\ \text{reactions}}} (\underline{W}+\underline{K})^T \begin{pmatrix} \underline{0} & \underline{0} & \underline{0} \\ \underline{0} & \underline{X}_L^{-1} & \underline{0} \\ \underline{0} & \underline{0} & \underline{0} \end{pmatrix} (\underline{W}+\underline{K}) = \underline{0} \quad (3-72)$$

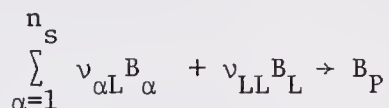
Equations (3-60), (3-70), (3-71) and (3-72) lead to the following equation for \underline{A}^{-1} in the complete reaction limit.

$$\underline{A}^{-1} = \begin{pmatrix} \underline{X}_S^{-1}-\underline{C}_{SS} & \{-(\underline{X}_S^{-1}-\underline{C}_{SS})\underline{v}_S + \underline{C}_{PS}^T \underline{v}_P\} \underline{v}_L^{-1} \\ (\underline{v}_L^{-1})^T \{ -\underline{v}_S^T (\underline{X}_S^{-1}-\underline{C}_{SS}) + \underline{v}_P^T \underline{C}_{PS} \} & \begin{pmatrix} (\underline{v}_L^{-1})^T \{ \underline{v}_S^T (\underline{X}_S^{-1}-\underline{C}_{SS}) \underline{v}_S - \underline{v}_P^T \underline{C}_{PS} \underline{v}_S \} \\ -\underline{v}_S^T \underline{C}_{PS}^T \underline{v}_P + \underline{v}_P^T (\underline{X}_P^{-1}-\underline{C}_{PP}) \underline{v}_P \} \underline{v}_L^{-1} \end{pmatrix} \end{pmatrix} \quad (3-73)$$

Although equation (3-73) appears somewhat complicated, it contains some important results and has two important limiting cases. Most important of these is that there are no contributions to \underline{A}^{-1} from direct

correlation functions involving limiting reactants. Also, it can be seen that \underline{A}^{-1} is symmetric as required.

If we look at a system with only solvation or association of components, then all reactions are of the form



where the B_{α} 's are solvents, B_L is the limiting reactant and B_P is the solvated product. The ν_P matrix is the identity matrix and

$$\underline{A}^{-1} = \begin{pmatrix} \underline{X}_S^{-1} - \underline{C}_{SS} & \{-(\underline{X}_S^{-1} - \underline{C}_{SS})\nu_S + \underline{C}_{PS}^T\}\nu_L^{-1} \\ (\nu_L^{-1})^T \{ \nu_S^T (\underline{X}_S^{-1} - \underline{C}_{SS})\nu_S - \underline{C}_{PS}\nu_S \} & -\nu_S^T \underline{C}_{PS}^T + (\underline{X}_P^{-1} - \underline{C}_{PP})\nu_L^{-1} \end{pmatrix} \quad (3-74)$$

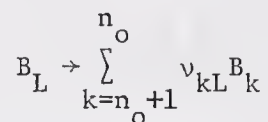
Equation (3-74) simplifies still further for systems with only either solvation or association. For the former, ν_L is the identity and

$$\underline{A}^{-1} = \begin{pmatrix} \underline{X}_S^{-1} - \underline{C}_{SS} & -(\underline{X}_S^{-1} - \underline{C}_{SS})\nu_S + \underline{C}_{PS}^T \\ \nu_S^T (\underline{X}_S^{-1} - \underline{C}_{SS})\nu_S - \underline{C}_{PS}\nu_S & -\nu_S^T \underline{C}_{PS}^T + (\underline{X}_P^{-1} - \underline{C}_{PP}) \end{pmatrix} \quad (3-75)$$

For the latter case, $\nu_S = \underline{0}$ and

$$\underline{A}^{-1} = \begin{pmatrix} \underline{X}_S^{-1} - \underline{C}_{SS} & \underline{C}_{PS}^T \nu_L^{-1} \\ (\nu_L^{-1})^T \underline{C}_{PS} & (\nu_L^{-1})^T (\underline{X}_P^{-1} - \underline{C}_{PP}) \nu_L^{-1} \end{pmatrix} \quad (3-76)$$

The other case of interest, and the case to be pursued more fully in later chapters, is that of complete dissociations, that is, reactions of the form



where B_L is the limiting reactant (dissociating component) and the B_k 's are product species. The solvents do not take part in the reactions ($\nu_S=0$). In this case, ν_L is the identity matrix and

$$\underline{A}^{-1} = \begin{pmatrix} \underline{X}_S^{-1} - \underline{C}_{SS} & \underline{C}_{PS}^T \underline{\nu}_P \\ \underline{\nu}_P^T \underline{C}_{PS} & \underline{\nu}_P^T (\underline{X}_P^{-1} - \underline{C}_{PP}) \underline{\nu}_P \end{pmatrix} \quad (3-77)$$

These results are quite simple to use, in fact evaluation of activities requires only simply quadratures, not the solution of partial differential equations as in the case of partial reactions.

CHAPTER 4

SOLUTIONS OF STRONG ELECTROLYTES

Introduction

O'Connell and DeGance (1975) give a formalism for expressing the fluctuation properties of electrolyte solutions (concentration derivatives of the chemical potential, partial molar volumes and compressibility) in terms of integrals of the radial distribution functions (Kirkwood-Buff solution theory, Kirkwood and Buff, 1951; O'Connell, 1971), and of nondivergent integrals of the direct correlation function. The formalism was based on a constraint on these radial distribution functions (Friedman and Ramanathan, 1970) which is not necessary to arrive at the desired results in the case of the direct correlation function integrals, but significantly affects results in the case of the radial distribution function integrals. The previous formalism was both rigorous and practical for properties of multicomponent solutions expressed in terms of radial distribution functions (assuming the constraint to be valid), but for the multisalt case yielded intractable equations when expressed in terms of direct correlation functions. This is primarily because the multicomponent charge neutrality conditions were mishandled.

The method used here parallels that of the previous chapter and yields equivalent results to those of O'Connell and DeGance for the single salt case, and quite simple results for multisalt systems. In addition, this method does not require that the constraints on the radial distribution function integrals be valid, although this situation is addressed further in Appendix G.

Material Balance Relationships among Salts, Solvents and Ions

In the case of strong (completely dissociating) electrolytes a more compact, but equivalent, set of matrices are used in the material balances and other relations than were used in the general formalism. This set is used because of the sparseness of the \underline{W} matrix and the fact that, with the salts as reference components (which is so in this chapter), the \underline{K} matrix is a zero matrix. The new matrices are defined below.

We look at a system of strong electrolytes dissolved in n_s solvents, where the total number of salts plus solvents is n_o and the total number of ions plus solvents is n ($n > n_o$ if independent salts are used - see Appendix H). The n_o components will be denoted by greek subscripts (α, β, \dots) and the n species by i, j, k, \dots .

We construct a matrix \underline{v} defined:

for solvents

$$v_{i\alpha} = \delta_{i\alpha} \quad \begin{array}{l} i = 1, \dots, s \\ \alpha = 1, \dots, s \end{array} \quad (4-1a)$$

and for electrolytes

$$v_{i\alpha} = \begin{array}{l} \text{the number of ions} \\ \text{of type } i \text{ in a molecule} \\ \text{of salt } \alpha. \end{array} \quad \begin{array}{l} i = s+1, \dots, n \\ \alpha = s+1, \dots, n \end{array} \quad (4-1b)$$

with all other elements being zeroes. In the notation of Chapter 3, the \underline{v} matrix can be written

$$\underline{v} = \begin{pmatrix} \underline{I} & \underline{0} \\ \underline{0} & \underline{v_D} \\ \underline{0} & \underline{v_I} \end{pmatrix} . \quad (4-2)$$

Such a system has $n - n_o$ constraints on its composition in terms of ions and solvents, and they may be represented by an n by $n - n_o$ matrix \underline{z}

having the property

$$\underline{v}^T \underline{z} = \underline{0} \quad (4-3a)$$

which gives

$$\underline{z} = \begin{pmatrix} \underline{0} \\ -(\underline{v}_D^{-1})^T \underline{v}_I^T \\ \underline{I} \end{pmatrix} \quad (4-3b)$$

The elements of \underline{z} include the ionic charges as well as any additional stoichiometric constraints. As these elements are not functions of composition, the \underline{z} matrix corresponds to the \underline{Z}_0 matrix defined previously.

In order to perform the desired projections, two more nonsquare matrices, \underline{u} and \underline{y} , are defined such that

$$\underline{v}^T \underline{u} = \underline{I} , \quad \underline{u}^T \underline{z} = \underline{0} \quad (4-4)$$

$$\underline{v}^T \underline{y} = \underline{I} , \quad \underline{y}^T \underline{z} \neq \underline{0} \quad (4-5)$$

where \underline{I} is an $n_o \times n_o$ identity matrix; $(\underline{I})_{ij} = \delta_{ij}$, $i, j = 1, \dots, n_o$. The \underline{u} matrix spans the same n_o -dimensional subspace of R^n as \underline{v} and is orthogonal to \underline{z} also. The form of \underline{u} will be derived below. The \underline{y} matrix is a very simple matrix, but is not orthogonal to \underline{z} . It has the form

$$\underline{y} = \begin{pmatrix} \underline{I} & \underline{0} \\ \underline{0} & -(\underline{v}_D^{-1})^T \\ \underline{0} & \underline{0} \end{pmatrix} \quad (4-6)$$

and from equations (4-5) and (4-6) we know that

$$\underline{u} = \underline{y} + \underline{z}b \quad (4-7)$$

where \underline{b} is an $(n-n_0) \times n_0$ coefficient matrix, the details of which are not important.

Finally, we define the $n \times n$ matrix

$$\underline{P} \equiv \underline{v}\underline{u}^T = \underline{u}\underline{v}^T = \underline{P}^T \quad (4-8)$$

where \underline{P} is the orthogonal projector for the component subspace, projecting perpendicular to the kernel and parallel to the image of \underline{v} . A property of \underline{P} is that for any matrix \underline{M} with a kernel that contains all the vectors of \underline{z} , i.e. $\underline{M}\underline{z} = \underline{0}$, then

$$\underline{M}\underline{P} = \underline{M} \quad (4-9)$$

Equations (4-8) and (4-9) also imply that

$$\underline{P}^2 = \underline{P} \quad (4-10a)$$

$$\underline{P}\underline{u} = \underline{u} \quad (4-10b)$$

$$\underline{P}\underline{v} = \underline{v} \quad (4-10c)$$

$$\underline{P}\underline{z} = \underline{0} \quad (4-10d)$$

and with equation (4-7)

$$\underline{P}\underline{y} = \underline{y} \quad (4-11)$$

All of these properties of \underline{P} will be used below.

The necessary matrices are easily constructed from the known \underline{v} matrix. Since \underline{u} and \underline{v} span the same subspace of the n -space, each column of \underline{u} must be a linear combination of the columns of \underline{v} . In all, the construction of \underline{u} from \underline{v} requires n_0^2 coefficients which make up the $n_0 \times n_0$ matrix, \underline{c} , such that

$$\underline{u} = \underline{v}\underline{c} \quad (4-12)$$

Using this identification in equation (4-4) gives

$$\underline{v}^T \underline{u} = \underline{v}^T \underline{v} \underline{c} = \underline{I} \quad (4-13a)$$

or

$$\underline{c} = (\underline{v}^T \underline{v})^{-1} \quad (4-13b)$$

This identification leads to¹

$$\underline{u} = \underline{v}(\underline{v}^T \underline{v})^{-1} \quad (4-14a)$$

or

$$\underline{u} = \begin{pmatrix} \underline{I} & \underline{0} \\ \underline{0} & \underline{v}_D (\underline{v}_D^T \underline{v}_D + \underline{v}_I^T \underline{v}_I)^{-1} \\ \underline{0} & \underline{v}_I (\underline{v}_D^T \underline{v}_D + \underline{v}_I^T \underline{v}_I)^{-1} \end{pmatrix} \quad (4-14b)$$

and

$$\underline{P} = \underline{v}(\underline{v}^T \underline{v})^{-1} \underline{v}^T \quad (4-15a)$$

or

$$\underline{P} = \begin{pmatrix} \underline{I} & \underline{0} & \underline{0} \\ \underline{0} & \underline{v}_D (\underline{v}_D^T \underline{v}_D + \underline{v}_I^T \underline{v}_I)^{-1} \underline{v}_D^T & \underline{v}_I (\underline{v}_D^T \underline{v}_D + \underline{v}_I^T \underline{v}_I)^{-1} \underline{v}_D^T \\ \underline{0} & \underline{v}_I (\underline{v}_D^T \underline{v}_D + \underline{v}_I^T \underline{v}_I)^{-1} \underline{v}_D^T & \underline{v}_I (\underline{v}_D^T \underline{v}_D + \underline{v}_I^T \underline{v}_I)^{-1} \underline{v}_I^T \end{pmatrix} \quad (4-15b)$$

The material balance relationship between the species and components is

$$\underline{N} = \underline{v} \underline{N}_O \quad (4-16a)$$

where \underline{N}_O is the vector of moles of solvents and salts (components). The

¹ $\underline{v}(\underline{v}^T \underline{v})^{-1} = (\underline{v})^{-1}$ iff \underline{v} is square (not possible here).

corresponding relations from species to components are

$$\underline{N}_O = \underline{u}^T \underline{N} = \underline{y}^T \underline{N} \quad (4-16b)$$

As before, the matrix expression relating species composition fluctuations and radial distribution function integrals is

$$\underline{A} = \underline{X} + \underline{X} \underline{H} \underline{X} \quad (4-17)$$

where the matrices \underline{A} , \underline{X} and \underline{H} have been defined previously. The species composition fluctuation matrix restricted to n_O degrees of freedom, \underline{A} , is given by

$$(\underline{A})_{\alpha\beta} = \left[\begin{array}{cc} (\underline{y})_{\alpha}^T + \frac{\partial \underline{\mu}_I^T}{\partial \mu_{O\alpha}} \Big|_{T,V,\mu_{O\gamma \neq \alpha}} & \underline{z}^T \end{array} \right] \underline{A}(\underline{y})_{\beta} \quad (4-18a)$$

where the elements of \underline{A} are given by

$$(\underline{A})_{\alpha\beta} = \frac{kT}{N} \frac{\partial N_{O\alpha}}{\partial \mu_{O\beta}} \Big|_{T,V,\mu_{O\gamma \neq \alpha}} = \frac{kT}{N} \frac{\partial N_{O\beta}}{\partial \mu_{O\alpha}} \Big|_{T,V,\mu_{O\gamma \neq \beta}} = (\underline{A})_{\beta\alpha} \quad (4-18b)$$

$\alpha, \beta = 1, \dots, n_O$

Equations (4-18) can be derived in a manner analogous to equation (3-37) using the methods of that chapter. Here, however, the matrices are slightly different (as shown above) and we explicitly define the salt chemical potentials by

$$\underline{\mu}_O = \underline{v}^T \underline{\mu} \quad (4-19)$$

where $\underline{\mu}$ is the vector of chemical potentials of solvents and ions. It

should be noted that although this is somewhat different from equations (2-4) and (2-5), the procedure followed in Chapter 3 still applies.

As in O'Connell and DeGance (1975), \underline{A} is nonsingular and can be inverted to give

$$(\underline{A}^{-1})_{\alpha\beta} = \frac{N}{kT} \frac{\partial \mu_{o\alpha}}{\partial N_{o\beta}} \bigg|_{T,V,N_{o\gamma \neq \beta}} = \frac{N}{kT} \frac{\partial \mu_{o\beta}}{\partial N_{o\alpha}} \bigg|_{T,V,N_{o\gamma \neq \alpha}} = (\underline{A}^{-1})_{\beta\alpha} \quad (4-20)$$

The radial distribution function integrals are related to \underline{A} by

$$\underline{A} = \left(\underline{y}^T + \frac{\partial \mu_I^T}{\partial \mu_o} \bigg|_{T,V} \underline{z}^T \right) (\underline{X} + \underline{XHX}) \underline{y} \quad (4-21)$$

This equation is much less formidable than it seems, since

$$\left(\underline{y}^T + \frac{\partial \mu_I^T}{\partial \mu_o} \bigg|_{T,V} \underline{z}^T \right) (\underline{X} + \underline{XHX}) \underline{z} = \underline{0} \quad (E-11)$$

or

$$\frac{\partial \mu_I^T}{\partial \mu_o} \bigg|_{T,V} = -\underline{y}^T (\underline{X} + \underline{XHX}) \underline{z} \{ \underline{z}^T (\underline{X} + \underline{XHX}) \underline{z} \}^{-1} \quad (4-22)$$

This allows us to rearrange equation (4-21) to¹

$$\underline{A} = \underline{y}^T \{ \underline{I} - (\underline{X} + \underline{XHX}) \underline{z} [\underline{z}^T (\underline{X} + \underline{XHX}) \underline{z}]^{-1} \underline{z}^T \} (\underline{X} + \underline{XHX}) \underline{y} \quad (4-23)$$

Of course, \underline{A}^{-1} is just the inverse of the right hand side of (4-23).

¹ See Appendix G for certain simplifications.

The set of equations that equation (4-23) represents can be solved by simple quadrature, as opposed to the more complex method required to solve the system of partial differential equations given in equation (3-57). However, even these quadratures are involved due to the multiple matrix operations (especially inversions) which need performed at every quadrature point. This difficulty can be alleviated if the dimensionality of the matrices are small enough to allow doing the matrix manipulations analytically. An example of the analytical method is given below. Thus, as before, the direct correlation approach should be of greater practical value. It has been shown (Gubbins and O'Connell, 1974; Brelvi and O'Connell, 1973, 1975) that direct correlation function integrals are insensitive to angle-dependent forces and yield excellent correlation and prediction of the properties of gases dissolved in various liquids, including water (Mathias and O'Connell, 1980a,b).

Formulation in Terms of Direct Correlation Functions

O'Connell and DeGance (1975) showed how expressions for single salts which were simple functions of nondivergent direct correlation function integrals could be attained. However, due to incomplete expressions for charge neutrality and composition constraints, this simplicity disappeared in the multisalt systems. An ancillary effect of this oversight was that some terms were stated to be included, but, in fact, are not.¹ The following results are considerably simpler.

¹ On pages 767 and 777 of O'Connell and DeGance (1975), it is noted that all terms of order (M-1) and less in the divergent integrals are preserved. In fact, only the first order terms remain.

Recognizing that the direct correlation function integrals of ions are divergent, we return to the definitions of the direct correlation functions themselves. For species of type i and j

$$c_{ij}(r_{12}) \equiv h_{ij}(r_{12}) - \sum_{k=1}^n \int h_{ik}(r_{23}) \rho_k c_{kj}(r_{13}) d\mathbf{r}_3 \quad (4-24)$$

In order to perform the transformations necessary to attain the desired matrix relations, both $c_{ij}(r_{12})$ and $h_{ij}(r_{12})$ must be integrable. However, $c_{ij}(r_{12})$ has a long range limit (O'Connell and DeGance, 1975) of

$$\lim_{r \rightarrow \infty} c_{ij}(r_{12}) = \frac{z_i z_j e^2}{\epsilon k T r_{12}} \quad (4-25)$$

which has a divergent integral over volume. Here, e is the charge on an electron and ϵ , the bulk dielectric constant of the solvent mixture. The presence of the $z_i z_j$ factor in equation (4-25) causes these portions of the direct correlation functions to lie in the kernel of the projection operator, \underline{P} . Therefore, these divergences can be removed in the process of projecting the species composition fluctuation matrix. We now write $c_{ij}(r)$ as the sum of a nondivergent part, $c_{ij}^o(r)$, and the divergent, long-range limit, giving

$$c_{ij}(r) = c_{ij}^o(r) + \frac{z_i z_j e^2}{\epsilon k T r} \quad (4-26)$$

Substituting equation (4-26) into (4-24) and operating from the right with \underline{P} gives

$$\sum_{j=1}^n c_{ij}^o(r_{12})(\underline{P})_{jk} + \sum_{j=1}^n \frac{z_i e^2}{\epsilon k T r} z_j (\underline{P})_{jk} = \sum_{j=1}^n h_{ij}(r_{12})(\underline{P})_{jk}$$

$$- \sum_{\ell=1}^n \int h_{i\ell}(r_{23}) \rho_{\ell} \left(\sum_{j=1}^n c_{\ell j}^o(r_{13}) (\underline{P})_{jk} + \sum_{j=1}^n \frac{z_{\ell} e^2}{\epsilon k T r} z_j (\underline{P})_{jk} \right) d\underline{r}_3 \quad (4-27)$$

Since the vector of species charges (the z_j 's) is in the space spanned by \underline{z} , we have by equation (4-10d)

$$\sum_{j=1}^n z_j (\underline{P})_{jk} = 0 \quad (4-28)$$

Use of this relation in equation (4-27) simplifies it to

$$\begin{aligned} \sum_{j=1}^n c_{ij}^o(r_{12}) (\underline{P})_{jk} &= \sum_{j=1}^n h_{ij}(r_{12}) (\underline{P})_{jk} - \sum_{j=1}^n \sum_{\ell=1}^n \left(\int h_{i\ell}(r_{23}) \rho_{\ell} \right. \\ &\quad \left. \times c_{\ell j}^o(r_{13}) d\underline{r}_3 \right) (\underline{P})_{jk} \end{aligned} \quad (4-29a)$$

or, after Fourier transforming,

$$\underline{C}^o \underline{P} = \underline{H} \underline{P} - \underline{H} \underline{X} \underline{C}^o \underline{P} \quad (4-29b)$$

where

$$(\underline{C}^o)_{ij} \equiv \frac{N}{V} \int c_{ij}^o(r; \rho, T) d\underline{r} \quad (4-29c)$$

Pre-multiplying equation (4-29b) by \underline{X} and rearranging gives, with equation (4-17)

$$\underline{X} \underline{H} \underline{P} = \underline{A} \underline{C}^o \underline{P}$$

Adding \underline{P} to both sides and using $\underline{A} \underline{X}^{-1} \underline{P} = \underline{P} + \underline{X} \underline{H} \underline{P}$, we find

$$\underline{A} (\underline{X}^{-1} - \underline{C}^o) \underline{P} = \underline{P} \quad (4-30)$$

which is nearly identical to equation (3-52).

We project to component variables by first pre-multiplying equation

$$(4-30) \text{ by } \left(\begin{array}{c|c} \underline{y}^T + \frac{\partial \underline{\mu}_I^T}{\partial \underline{\mu}_O} & \underline{z}^T \\ \hline & \end{array} \right)_{T,V}, \text{ the right hand side simplifying via}$$

equations (4-10d) and (4-11).

$$\left(\begin{array}{c|c} \underline{y}^T + \frac{\partial \underline{\mu}_I^T}{\partial \underline{\mu}_O} & \underline{z}^T \\ \hline & \end{array} \right)_{T,V} \underline{A} (\underline{X}^{-1} - \underline{C}^O) \underline{P} = \underline{u}^T \quad (4-31)$$

Equation (E-11) makes it clear that $\left(\begin{array}{c|c} \underline{y}^T + \frac{\partial \underline{\mu}_I^T}{\partial \underline{\mu}_O} & \underline{z}^T \\ \hline & \end{array} \right)_{T,V} \underline{A}$ has the

required characteristics of matrix \underline{M} in equation (4-9). Thus we know

$$\left(\begin{array}{c|c} \underline{y}^T + \frac{\partial \underline{\mu}_I^T}{\partial \underline{\mu}_O} & \underline{z}^T \\ \hline & \end{array} \right)_{T,V} \underline{AP} = \left(\begin{array}{c|c} \underline{y}^T + \frac{\partial \underline{\mu}_I^T}{\partial \underline{\mu}_O} & \underline{z}^T \\ \hline & \end{array} \right)_{T,V} \underline{A} \quad (4-32)$$

Substituting this into equation (4-31) and using (4-8) gives

$$\left(\begin{array}{c|c} \underline{y}^T + \frac{\partial \underline{\mu}_I^T}{\partial \underline{\mu}_O} & \underline{z}^T \\ \hline & \end{array} \right)_{T,V} \underline{Au} \underline{v}^T (\underline{X}^{-1} - \underline{C}^O) \underline{P} = \underline{u}^T \quad (4-33)$$

Post-multiplying by \underline{v} and successively using equations (4-10a), (4-11)

and (4-18), equation (4-33) becomes

$$\underline{Av}^T (\underline{X}^{-1} - \underline{C}^O) \underline{v} = \underline{I} \quad (4-34a)$$

or

$$\underline{A}^{-1} = \underline{v}^T (\underline{X}^{-1} - \underline{C}^O) \underline{v} \quad (4-34b)$$

Equation (4-34b) provides a very straightforward relationship between the desired macroscopic salt properties (elements of \underline{A}^{-1}) and the molecular direct correlation function integrals for the ions and solvents. Note that both \underline{v} and \underline{X}^{-1} are both simple and well-known matrices and that all solvent-solvent relationships are left totally unaffected by these transformations. This result is identical to equation (3-77), as required.

Thermodynamic Properties

The general matrix relationships between measurable thermodynamic properties and the correlation function integrals are summarized here. We choose to work with the mean ionic salt properties, such as the mean ionic activity coefficient on the mole fraction scale,

$$\begin{aligned} \ln \gamma_{\pm\alpha} &= \frac{1}{v_{\alpha}} \left(\sum_{i=s+1}^n v_{i\alpha} \ln \gamma_i \right) = \frac{1}{v_{\alpha} kT} \left(\sum_{i=s+1}^n v_{i\alpha} (\mu_i - \mu_i^0 - kT \ln N_i/N) \right) \\ v_{\alpha} \ln \gamma_{\pm\alpha} &= \frac{\mu_o - \mu_{o\alpha}^0}{kT} - \sum_{i=s+1}^n v_{i\alpha} \ln \left(\sum_{\gamma=1}^{n_o} v_{i\gamma} N_{o\gamma}/N \right) \end{aligned} \quad (4-35)$$

with

$$v_{\alpha} = \sum_{i=1}^n v_{i\alpha} \quad \alpha=s+1, \dots, n_o$$

Here we have tacitly assumed that $\underline{\mu}_o^0 = \underline{v}\underline{\mu}^0$, which are the usual standard states chosen for salt solutions. Differentiating with respect to $N_{o\beta}$ yields (Friedman and Ramanathan, 1970)

$$N v_{\alpha} \left. \frac{\partial \ln \gamma_{\pm\alpha}}{\partial N_{o\beta}} \right|_{T,P,N_{o\gamma \neq \beta}} = \frac{N}{kT} \left. \frac{\partial \mu_{o\alpha}}{\partial N_{o\beta}} \right|_{T,P,N_{o\gamma \neq \beta}} - \sum_{i=s+1}^n \frac{v_{i\alpha} v_{i\beta}}{x_i} + v_{\alpha} v_{\beta} \quad (4-36)$$

where,

$$x_i = N_i/N$$

If equation (4-36) is restricted to salts of two different ions (+ and -) and to systems without ions common to different salts, it becomes

$$Nv_\alpha \left. \frac{\partial \ln \gamma_{\pm\alpha}}{\partial N_{o\beta}} \right|_{T,P,N_{o\gamma \neq \beta}} = \left. \frac{N}{kT} \frac{\partial \mu_{o\alpha}}{\partial N_{o\beta}} \right|_{T,P,N_{o\gamma \neq \beta}} - \frac{v_\alpha N}{N_{o\alpha}} \delta_{\alpha\beta} + v_\alpha v_\beta \quad (4-37)$$

The partial molar volumes are, for solvents

$$\begin{aligned} \bar{v}_{oi} &= \left. \frac{\partial V}{\partial N_{oi}} \right|_{T,P,N_{o\beta \neq i}} = \left. \frac{\partial \mu_{oi}}{\partial P} \right|_{T,N_o} = \left. \frac{\partial (\mu_{oi}^o + RT \ln x_{oi} \gamma_{oi})}{\partial P} \right|_{T,N_o} \\ &= \bar{v}_{oi}^o + RT \left. \frac{\partial \ln \gamma_{oi}}{\partial P} \right|_{T,N_o} \quad \begin{matrix} i=1,\dots,s \\ \beta=1,\dots,n_o \end{matrix} \quad (4-38a) \end{aligned}$$

and for salts

$$\begin{aligned} \bar{v}_{o\alpha} &= \left. \frac{\partial V}{\partial N_{o\alpha}} \right|_{T,P,N_{o\beta \neq \alpha}} = \left. \frac{\partial \mu_{o\alpha}}{\partial P} \right|_{T,N_o} = \left. \frac{\partial (\mu_{o\alpha}^o + v_\alpha RT \ln x_{\pm\alpha} \gamma_{\pm\alpha})}{\partial P} \right|_{T,N_o} \\ &= \bar{v}_{o\alpha}^o + v_\alpha RT \left. \frac{\partial \ln \gamma_{\pm\alpha}}{\partial P} \right|_{T,N_o} \quad \begin{matrix} \alpha=s+1,\dots,n_o \\ \beta=1,\dots,n_o \end{matrix} \quad (4-38b) \end{aligned}$$

The partial molar volumes are related to the \underline{A} matrix by the relation

$$\left. \frac{\partial P/RT}{\partial \rho_{o\alpha}} \right|_{T,\rho_{o\beta \neq \alpha}} = \frac{\bar{v}_{o\alpha}}{\kappa_T RT} = (\underline{A}^{-1} \underline{u} \underline{X} i)_\alpha \quad \alpha=1,\dots,n_o \quad (4-39)$$

where $\rho_{o\alpha} \equiv N_{o\alpha}/V$, κ_T is the isothermal compressibility and \underline{i} is a column vector of n ones. Also,

$$\left. \frac{\partial P/RT}{\partial \rho} \right|_{T, \underline{N}} = \frac{1}{\rho \kappa_T RT} = \underline{i} \underline{X}^T \underline{u} \underline{A}^{-1} \underline{u}^T \underline{X} \underline{i} \quad (4-40)$$

where ρ is the molar density for the ions plus solvents, $\rho \equiv N/V$.

Further,

$$\underline{G} = \underline{A}^{-1} - \underline{V} - \underline{v} \underline{X}^{-1} \underline{v} + \underline{v} \underline{1} \underline{v} \quad (4-41)$$

where

$$(\underline{G})_{\alpha\beta} = N v_{\alpha} \left. \frac{\partial \ln \gamma_{\pm\alpha}}{\partial N_{o\beta}} \right|_{T, P, N_{o\gamma \neq \beta}} = (\underline{G})_{\beta\alpha} \quad \alpha, \beta = 1, \dots, n_o \quad (4-42)$$

$$(\underline{V})_{\alpha\beta} = \frac{\rho \bar{v}_{o\alpha} \bar{v}_{o\beta}}{\kappa_T RT} \quad \alpha, \beta = 1, \dots, n_o \quad (4-43)$$

and $\underline{1}$ is an $n \times n$ matrix of ones.

All of the desired properties can then be obtained from correlation function integrals using equations (4-34) and (4-39) to (4-41). The expressions in terms of the $(\underline{H})_{ij}$ are complex (O'Connell and DeGance, 1975; Friedman and Ramanathan, 1970) whereas they are simple when the $(\underline{C}^o)_{ij}$ are used.

$$\frac{1}{\rho \kappa_T RT} = 1 - \underline{i}^T \underline{X} \underline{C}^o \underline{X} \underline{i} = \sum_{i=1}^n \sum_{j=1}^n x_i x_j [1 - (\underline{C}^o)_{ij}] \quad (4-44)$$

$$\frac{\bar{v}_{o\alpha}}{\kappa_T RT} = \underline{v}^T (\underline{I} - \underline{C}^o \underline{X}) \underline{i} = \sum_{i=1}^n v_{i\alpha} \sum_{j=1}^n x_j [1 - (\underline{C}^o)_{ij}] \quad \alpha = 1, \dots, n_o \quad (4-45)$$

$$\frac{1}{\rho \kappa_T RT} (\underline{G})_{\alpha\beta} = \sum_{i=1}^n \sum_{j=1}^n v_{i\alpha} v_{j\beta} \sum_{k=1}^n \sum_{\ell=1}^n x_k x_{\ell} \{ [1 - (\underline{C}^o)_{k\ell}] [1 - (\underline{C}^o)_{ij}] \}$$

$$- [1-(\underline{C}^0)_{ik}] [1-(\underline{C}^0)_{jl}]] \quad (4-46)$$

These results are in the same form as for nonelectrolytes (Mathias and O'Connell, 1980a,b). Equations (4-45) and (4-46) are much less formidable than they appear due to the sparseness of \underline{v} and cancellations. For salts of two different ions, the double summation over i and j leads to, at most, four terms.

Since they can be modeled well in nonelectrolyte solutions, we also believe it is useful to work with fluctuation matrices in terms of density rather than moles. We know that for both salts and solvents,

$$\left. \frac{\rho}{kT} \frac{\partial \mu_{o\alpha}}{\partial \rho_{o\beta}} \right|_{T, \rho_{o\gamma \neq \beta}} = \left. \frac{N}{kT} \frac{\partial \mu_{o\alpha}}{\partial N_{o\beta}} \right|_{T, V, N_{o\gamma \neq \beta}} = (\underline{A})_{\alpha\beta}^{-1} = (\underline{A})_{\alpha\beta}^{-1} \quad (4-47)$$

Defining an activity coefficient, y , based on concentration or molar density,

$$\mu_{o\alpha} \equiv \mu_{o\alpha}^0 + RT \ln \rho_{o\alpha} y_{o\alpha} \quad \text{for solvents} \quad (4-48)$$

$$\equiv \mu_{o\alpha}^0 + v_{\alpha} RT \ln \rho_{\pm\alpha} y_{\pm\alpha} \quad \text{for salts}$$

We can write

$$\underline{G}' = \underline{A}^{-1} - \underline{v} \underline{X}^{-1} \underline{v} \quad (4-49)$$

where

$$(\underline{G}')_{\alpha\beta} = \rho \left. \frac{\partial \ln y_{o\alpha}}{\partial \rho_{o\beta}} \right|_{T, \rho_{o\gamma \neq \beta}} = (\underline{G}')_{\beta\alpha} = - (\underline{v}^T \underline{C}^0 \underline{v})_{\alpha\beta} \quad (4-50a)$$

and

$$\rho_{o\beta} = N_{o\beta}/V \quad (4-50b)$$

Note that for $\alpha = \text{salt}$, we write $v_{\alpha} \ln y_{\pm\alpha}$ instead of $\ln y_{o\alpha}$. Previous success (Mathias and O'Connell, 1980a,b) in modeling $(\underline{C}^0)_{ij}$ for non-electrolytes may indicate that the same may be done for electrolyte systems. In this case, the expressions should include short-range, infinite dilution and Debye-Hueckel contributions. However, these are ion-specific, not salt-specific.

Single-Salt, Single-Solvent System

The simplest example of salt solutions yields results obtained by less elaborate methods. However, for illustrative purposes, we will use the above method to derive these expressions. In this system, the solvent is indexed 1 and the salt, with ions + and -, is indexed 2. Since the choice is arbitrary, we chose + as the dependent and - as the independent ions. This choice gives, for equations (4-2) and (4-6)

$$\underline{v} = \begin{pmatrix} 1 & 0 \\ 0 & v_+ \\ 0 & v_- \end{pmatrix} \quad \underline{y} = \begin{pmatrix} 1 & 0 \\ 0 & 1/v_+ \\ 0 & 0 \end{pmatrix} \quad (4-51a)$$

The \underline{z} matrix is, from equation (4-3b),

$$\underline{z} = \begin{pmatrix} 0 \\ -v_-/v_+ \\ 1 \end{pmatrix} \quad (4-51b)$$

If we multiply \underline{z} by z_- , it becomes

$$\underline{zz}_- = \begin{pmatrix} 0 \\ -v_- z_- / v_+ \\ z_- \end{pmatrix} = \begin{pmatrix} 0 \\ z_+ \\ z_- \end{pmatrix}$$

which shows that \underline{z} is indeed parallel to the vector of ionic charges as required in equation (4-27).

First, we give matrix \underline{A} in terms of $(\underline{H})_{ij}$. Equation (4-23) gives

$$(\underline{A})_{11} = x_{o1} + x_{o1}^2 \left[(\underline{H})_{11} - \frac{x_+ x_- \{ (\underline{H})_{1+} - (\underline{H})_{1-} \}^2}{v x_{o2} + x_+ x_- \{ (\underline{H})_{++} - 2(\underline{H})_{+-} + (\underline{H})_{--} \}} \right] \quad (4-52a)$$

$$\begin{aligned} (\underline{A})_{12} = (\underline{A})_{21} = x_{o1} x_{o2} & \left[x_+ (\underline{H})_{1+} + x_- (\underline{H})_{1-} + x_+ x_- (\underline{H})_{1+} \{ (\underline{H})_{--} - (\underline{H})_{+-} \} \right. \\ & \left. + x_+ x_- (\underline{H})_{1-} \{ (\underline{H})_{++} - (\underline{H})_{+-} \} \right] \div \left[v x_{o2} + x_+ x_- \{ (\underline{H})_{++} - 2(\underline{H})_{+-} + (\underline{H})_{--} \} \right] \end{aligned} \quad (4-52b)$$

$$\begin{aligned} (\underline{A})_{22} = x_{o2}^2 & \left[1 + x_+ (\underline{H})_{++} + x_- (\underline{H})_{--} + x_+ x_- \{ (\underline{H})_{++} (\underline{H})_{--} - (\underline{H})_{+-}^2 \} \right] \\ & \div \left[x_{o2} + x_+ x_- \{ (\underline{H})_{++} - 2(\underline{H})_{+-} + (\underline{H})_{--} \} \right] \end{aligned} \quad (4-52c)$$

where

$$x_{o1} = N_{o1}/N = N_1/N = x_1 \quad (4-53a)$$

$$x_{o2} = N_{o2}/N = N_2/vN = x_+/v_+ = x_-/v_- \quad (4-53b)$$

and

$$v = v_+ + v_- \quad (4-54)$$

Interchanging the + and - subscripts does not affect the results. This must be true since the choice of dependent and independent ion was arbitrary. The \underline{A}^{-1} elements can be determined by inversion.

For the direct correlation function integrals, the elements of \underline{A}^{-1} can be determined directly from equation (4-34b). From equation (4-20), we now find

$$\left. \frac{N}{kT} \frac{\partial \mu_{o1}}{\partial N_{o1}} \right|_{T,V,N_{o2}} = \frac{1}{x_{o1}} - (\underline{C}^o)_{11} \quad (4-55)$$

$$= \frac{x_{o2}^2 \{1 + x_+ (\underline{H})_{++} + x_- (\underline{H})_{--} + x_+ x_- [(\underline{H})_{++} - (\underline{H})_{+-}]^2\}}{\text{denom.}}$$

$$\left. \frac{N}{kT} \frac{\partial \mu_{o1}}{\partial N_{o2}} \right|_{T,V,N_{o1}} = \left. \frac{N}{kT} \frac{\partial \mu_{o2}}{\partial N_{o1}} \right|_{T,V,N_{o2}} = -\{v_+ (\underline{C}^o)_{1+} + (\underline{C}^o)_{1-} v_-\} \equiv -v C_{12}^o$$

$$= -x_{o1} x_{o2} \{x_+ (\underline{H})_{1+} + x_- (\underline{H})_{1-} + x_+ x_- \{ [(\underline{H})_{--} - (\underline{H})_{+-}] (\underline{H})_{1+} \\ + [(\underline{H})_{++} - (\underline{H})_{+-}] (\underline{H})_{1-} \} \} \div (\text{denom.}) \quad (4-56)$$

$$\left. \frac{N}{kT} \frac{\partial \mu_{o2}}{\partial N_{o2}} \right|_{T,V,N_{o1}} = \frac{1}{x_{o2}} - \{v_+^2 (\underline{C}^o)_{++} - 2v_+ v_- (\underline{C}^o)_{+-} + v_-^2 (\underline{C}^o)_{--}\} \equiv \frac{1}{x_{o2}} - v^2 C_{22}^o$$

$$= \left\{ \{x_{o1} + x_{o2}^2 (\underline{H})_{11}\} \{x_{o2} + x_+ x_- [(\underline{H})_{++} (\underline{H})_{--} - (\underline{H})_{+-}^2]\} \right. \\ \left. - x_+ x_- x_{o1}^2 [(\underline{H})_{1+} - (\underline{H})_{1-}]^2 \right\} \div (\text{denom.}) \quad (4-57)$$

where

$$\text{denom.} = \{x_{o1} + x_{o1}^2 (\underline{H})_{11}\} \{1 + x_+ (\underline{H})_{++} + x_- (\underline{H})_{--} + x_+ x_- [(\underline{H})_{++} (\underline{H})_{--} - (\underline{H})_{+-}^2]\} \\ - x_{o1} x_{o2}^2 \{v x_{o2} x_+ (\underline{H})_{1+}^2 + x_- (\underline{H})_{1-}^2 + x_+ x_- [(\underline{H})_{1+}^2 (\underline{H})_{--} + (\underline{H})_{1-}^2 (\underline{H})_{++} \\ - 2(\underline{H})_{1+} (\underline{H})_{1-} (\underline{H})_{+-}]\} \quad (4-58)$$

Then

$$\frac{1}{\rho \kappa_{RT}} = x_{o1}^2 (1 - C_{11}^o) + 2v x_{o1} x_{o2} (1 - C_{12}^o) + v^2 x_{o2}^2 (1 - C_{22}^o) \quad (4-59)$$

$$\bar{v}_{o2}/\kappa_{T}^{RT} = v\{x_{o1}(1-C_{12}^o) + vx_{o2}(1-C_{22}^o)\} \quad (4-60)$$

$$\left. \frac{Nv}{\rho\kappa_{T}^{RT}} \frac{\partial \ln \gamma_{\pm}}{\partial N_{o2}} \right|_{T,P,N_{o1}} = (vx_{o1}^2) \{ (1-C_{11}^o)(1-C_{22}^o) - (1-C_{12}^o)^2 \} \quad (4-61)$$

$$\left. \rho v \frac{\partial \ln \gamma_{\pm}}{\partial \rho_{o2}} \right|_{T,\rho_{o1}} = -v^2 C_{22}^o \quad (4-62)$$

The direct correlation function integrals can be related to infinite dilution values and the Debye-Hueckel limiting law expressions.

The correct expressions are

$$v \ln \gamma_{\pm} = -S_{\gamma} (vx_{o2})^{1/2} + O(x_{o2}) \quad (4-63)$$

where

$$S_{\gamma} = \pi^{1/2} N_A^2 \left(\frac{e^2}{\epsilon_1 RT} \left\{ \sum v_i z_i^2 \right\} \right)^{3/2} \quad (4-64)$$

with ϵ_1 the solvent dielectric constant, N_A , Avagadro's number and e , the unit charge. Then (Redlich and Meyer, 1964)

$$\bar{v}_{o2} - \bar{v}_{o2}^{\infty} = vRT \left. \frac{\partial \ln \gamma_{\pm}}{\partial P} \right|_{T,N_{o1},N_{o2}} \quad (4-65a)$$

$$= \frac{3}{2} S_v (\rho_{o1} x_{o2})^{1/2} + O(x_{o2}) \quad (4-65b)$$

where

$$S_v = S_{\gamma}^{RT} \left(\left. \frac{\partial \ln \epsilon_1}{\partial P} \right|_T - \frac{\kappa_1}{3} \right) \quad (4-66)$$

and κ_1 is the solvent isothermal compressibility. The solution isothermal compressibility defines the apparent molar compressibility, ϕ_k , (Gucker, 1933).

$$\kappa_T = x_{o1}\kappa_1\rho / \rho_{o1} + x_{o2}\phi_k\rho \quad (4-67)$$

where

$$x_{o1} + vx_{o2} = 1$$

and

$$\phi_k - \phi_k^o = \frac{2}{3} S_k (\rho x_{o2})^{\frac{1}{2}} + O(x_{o2}) \quad (4-68a)$$

with

$$S_k = \frac{S_Y RT}{4} \left[\kappa_1^2 + 2 \frac{\partial \kappa_1}{\partial P} \Big|_T - 6 \kappa_1 \frac{\partial \ln \epsilon_1}{\partial P} \Big|_T + 9 \left(\frac{\partial \ln \epsilon_1}{\partial P} \Big|_T \right)^2 - 6 \frac{\partial^2 \ln \epsilon_1}{\partial P^2} \Big|_T \right] \quad (4-68b)$$

(General expressions for the multisalt case are found in Appendix I.)

These equations yield

$$1-C_{11}^o = \frac{1}{\rho_1 \kappa_1 RT} (1 + vx_{o2}) - \left(\frac{\phi_k^o x_{o2}}{\kappa_1^2 RT} + \frac{S_V}{\kappa_1 RT} + \frac{S_Y}{2} + \frac{2}{3} \frac{S_k}{\kappa_1^2 RT} \right) \rho_1^{\frac{1}{2}} x_{o2}^{3/2} + O(x_{o2}^2) \quad (4-69)$$

$$1-C_{12}^o = \frac{\bar{v}_2^\infty}{\kappa_1 RT} + \frac{3}{2} \frac{S_Y}{v \kappa_1} \frac{\partial \ln \epsilon_1}{\partial P} \Big|_T (\rho_1 x_{o2})^{\frac{1}{2}} + O(x_{o2}) \quad (4-70)$$

$$1-C_{22}^o = - \frac{S_Y}{2v^2} \left(\frac{\rho_1}{x_{o2}} \right)^{\frac{1}{2}} + \text{constant} + O(x_{o2}^{\frac{1}{2}}) \quad (4-71)$$

Double-Salt, Single-Solvent Case

Assuming the two salts contain different ions, we write the \underline{v} , \underline{y} and \underline{z} matrices, which are simple extensions of the one-salt case. Again we choose the positive ions as dependent, and the negative ions as independent.

$$\underline{v} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & v_{2+} & 0 \\ 0 & 0 & v_{3+} \\ 0 & v_{2-} & 0 \\ 0 & 0 & v_{3-} \end{pmatrix}, \quad \underline{y} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1/v_{2+} & 0 \\ 0 & 0 & 1/v_{3+} \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \underline{z} = \begin{pmatrix} 0 & 0 \\ -v_{2-}/v_{2+} & 0 \\ 0 & -v_{3-}/v_{3+} \\ 1 & 0 \\ 0 & 1 \end{pmatrix}$$

(4-72)

Multiplying the first column of \underline{z} by z_{2-} , and the second by z_{3-} , we again get the matrix of ionic charges for salts 2 and 3. The \underline{A} matrix, in terms of total correlation function integrals, becomes quite complex. In terms of component matrices, it is

$$\underline{A} = \begin{pmatrix} x_{o1} + x_{o1}^2(\underline{H})_{11} & x_{o1}x_{o2}(\underline{H})_{12+} & x_{o1}x_{o3}(\underline{H})_{13+} \\ x_{o1}x_{o2}(\underline{H})_{12+} & x_{o2}/v_{2+} + x_{o2}^2(\underline{H})_{2+2+} & x_{o2}x_{o3}(\underline{H})_{2+3+} \\ x_{o1}x_{o3}(\underline{H})_{13+} & x_{o2}x_{o3}(\underline{H})_{2+3+} & x_{o3}/v_{3+} + x_{o3}^2(\underline{H})_{3+3+} \end{pmatrix}$$

$$- \begin{pmatrix} x_{o1}x_{2-}\{(\underline{H})_{12-} - (\underline{H})_{12+}\} & x_{o1}x_{3-}\{(\underline{H})_{13-} - (\underline{H})_{13+}\} \\ x_{2-}/v_{2+} + x_{o2}x_{2-}\{(\underline{H})_{2+2-} - (\underline{H})_{2+2+}\} & x_{o2}x_{3-}\{(\underline{H})_{2+3-} - (\underline{H})_{2+3+}\} \\ x_{2-}x_{o3}\{(\underline{H})_{3+2-} - (\underline{H})_{2+3+}\} & \frac{x_{3-}}{v_{3+}} + x_{o3}x_{3-}\{(\underline{H})_{3+3-} - (\underline{H})_{3+3+}\} \end{pmatrix}$$

$$\begin{aligned}
& \times \begin{pmatrix} v_{3-}x_{3-}/v_{3+} + x_{3-}^2 \{ (\underline{H})_{3+3+} + (\underline{H})_{3-3-} - 2(\underline{H})_{3+3-} \} \\ \\ -x_{2-}x_{3-} \{ (\underline{H})_{2+3+} + (\underline{H})_{2-3-} - (\underline{H})_{2+3-} - (\underline{H})_{3+2-} \} \\ \\ -x_{2-}x_{3-} \{ (\underline{H})_{2+3+} + (\underline{H})_{2-3-} - (\underline{H})_{2+3-} - (\underline{H})_{2-3+} \} \\ \\ \frac{v_{2-}}{v_{2+}} x_{2-} + x_{2-}^2 \{ (\underline{H})_{2+2+} + (\underline{H})_{2-2-} - 2(\underline{H})_{2+2-} \} \end{pmatrix} \\
& \times \begin{pmatrix} x_{o1}x_{2-} \{ (\underline{H})_{12-} - (\underline{H})_{12+} \} & x_{o1}x_{3-} \{ (\underline{H})_{13-} - (\underline{H})_{13+} \} \\ \frac{x_{2-}}{v_{2+}} + x_{o2}x_{2-} \{ (\underline{H})_{2+2-} - (\underline{H})_{2+2+} \} & x_{o2}x_{3-} \{ (\underline{H})_{2+3-} - (\underline{H})_{2+3+} \} \\ x_{2-}x_{o3} \{ (\underline{H})_{3+2-} - (\underline{H})_{2+3+} \} & \frac{x_{3-}}{v_{3+}} + x_{o3}x_{3-} \{ (\underline{H})_{3+3-} - (\underline{H})_{3+3+} \} \end{pmatrix}^T \\
& \div \{ v_{2-}x_{2-}/v_{2+} + x_{2-}^2 [(\underline{H})_{2+2+} + (\underline{H})_{2-2-} - 2(\underline{H})_{2+2-}] \} \{ v_{3-}x_{3-}/v_{3+} + x_{3-}^2 [(\underline{H})_{3+3+} \\
& + (\underline{H})_{3-3-} - 2(\underline{H})_{3+3-}] \} - x_{2-}^2 x_{3-}^2 \{ (\underline{H})_{2+3+} + (\underline{H})_{2-3-} - (\underline{H})_{2+3-} - (\underline{H})_{3+2-} \}^2
\end{aligned}
\tag{4-73}$$

The elements of \underline{A}^{-1} in terms of the total correlation function integrals must be determined by carrying out the matrix operations in equation (4-73) and then inverting the result. It is clear that this would be a very complex expression.

However, equations (4-34b) and (4-72) allow us to write the elements of \underline{A}^{-1} easily, in terms of the direct correlation function integrals. These elements are:

$$\left. \frac{N}{kT} \frac{\partial \mu_{o1}}{\partial N_{o1}} \right|_{T, V, N_{o2}, N_{o3}} = \frac{1}{x_{o1}} - c_{11}^o \tag{4-74}$$

$$\left. \frac{N}{kT} \frac{\partial \mu_{o1}}{\partial N_{o2}} \right|_{T,V,N_{o1},N_{o3}} = -v_2 C_{12}^o \quad (4-75)$$

$$\left. \frac{N}{kT} \frac{\partial \mu_{o2}}{\partial N_{o2}} \right|_{T,V,N_{o1},N_{o3}} = \frac{v_2}{x_{o2}} - v_2^2 C_{22}^o \quad (4-76)$$

and

$$\left. \frac{N}{kT} \frac{\partial \mu_{o2}}{\partial N_{o3}} \right|_{T,V,N_{o1},N_{o2}} = -v_2 v_3 C_{23}^o \quad (4-77)$$

where the $C_{\alpha\beta}^o$ ($\alpha, \beta=1,2$) above are defined in equations (4-56) and (4-57)

and

$$C_{23}^o = \frac{v_{2+}v_{3+}(\underline{C}^o)_{2+3+} + v_{2+}v_{3-}(\underline{C}^o)_{2+3-} + v_{2-}v_{3+}(\underline{C}^o)_{2-3+} + v_{2-}v_{3-}(\underline{C}^o)_{2-3-}}{v_2 v_3} \quad (4-78)$$

In the above equations, the other derivatives of the chemical potential may be found by simply interchanging subscripts 2 and 3 and defining C_{13}^o and C_{33}^o in a manner analogous to C_{12}^o and C_{22}^o . Expressions for the thermodynamic properties are the same as those of Friedman and Ramana- than only when the constraint

$$(\underline{X} + \underline{XHX})\underline{z} = \underline{0} \quad (4-79)$$

is assumed (for the results in this case, see Appendix G). The expressions in terms of the total correlations quickly grow cumbersome, but the expressions in terms of direct correlations remain unchanged. Since the matrix in terms of the $(\underline{H})_{ij}$ must be inverted, and because of the

complexity of the relationship between \underline{A} and the $(\underline{H})_{ij}$, we prefer to focus on the expressions using direct correlation function integrals, which avoid both complexities. Using equations (4-44) to (4-46), we find

$$\begin{aligned} \frac{1}{\rho\kappa_{\text{T}}^{\text{RT}}} = 1 - [x_{\text{o1}}^2 C_{11}^{\text{o}} + 2v_2 x_{\text{o1}} x_{\text{o2}} C_{12}^{\text{o}} + 2v_3 x_{\text{o1}} x_{\text{o3}} C_{13}^{\text{o}} + v_2^2 x_{\text{o2}}^2 C_{22}^{\text{o}} \\ + 2v_2 v_3 x_{\text{o2}} x_{\text{o3}} C_{23}^{\text{o}} + v_3^2 x_{\text{o3}}^2 C_{33}^{\text{o}}] \end{aligned} \quad (4-80)$$

$$\frac{\bar{v}_{\text{o2}}}{\kappa_{\text{T}}^{\text{RT}}} = 1 - v_2 [x_{\text{o1}} C_{12}^{\text{o}} + v_2 x_{\text{o2}} C_{22}^{\text{o}} + v_3 x_{\text{o3}} C_{23}^{\text{o}}] \quad (4-81)$$

$$\begin{aligned} \left(\frac{Nv_2}{\rho\kappa_{\text{T}}^{\text{RT}}} \right) \frac{\partial \ln \gamma_{\pm 2}}{\partial N_{\text{o2}}} \bigg|_{\text{T,P,N}_{\text{o}\gamma \neq 2}} = v_2^2 \{ [1 - C_{22}^{\text{o}}] [x_{\text{o2}}^2 (1 - C_{11}^{\text{o}}) + 2v_3 x_{\text{o1}} x_{\text{o3}} (1 - C_{13}^{\text{o}}) \\ + v_3^2 x_{\text{o3}}^2 (1 - C_{33}^{\text{o}})] - [x_{\text{o1}} (1 - C_{12}^{\text{o}}) + v_3 x_{\text{o3}} (1 - C_{23}^{\text{o}})]^2 \} \end{aligned} \quad (4-82)$$

$$\begin{aligned} \left(\frac{Nv_2}{\rho\kappa_{\text{T}}^{\text{RT}}} \right) \frac{\partial \ln \gamma_{\pm 2}}{\partial N_{\text{o3}}} \bigg|_{\text{T,P,N}_{\text{o}\gamma \neq 3}} = v_2 v_3 \{ [1 - C_{23}^{\text{o}}] [x_{\text{o1}}^2 (1 - C_{11}^{\text{o}}) + v_2 x_{\text{o1}} x_{\text{o2}} (1 - C_{12}^{\text{o}}) \\ + v_3 x_{\text{o1}} x_{\text{o3}} (1 - C_{13}^{\text{o}}) + v_2 v_3 x_{\text{o2}} x_{\text{o3}} (1 - C_{23}^{\text{o}})] \\ - [x_{\text{o1}} (1 - C_{12}^{\text{o}}) + v_2 x_{\text{o2}} (1 - C_{22}^{\text{o}})] [x_{\text{o1}} (1 - C_{13}^{\text{o}}) \\ + v_2 x_{\text{o3}} (1 - C_{33}^{\text{o}})] \} \end{aligned} \quad (4-83)$$

$$\rho v_2 \frac{\partial \ln \gamma_{\pm 2}}{\partial \rho_{\text{o2}}} \bigg|_{\text{T}, \rho_{\text{o}\gamma \neq 2}} = - v_2^2 C_{22}^{\text{o}} \quad (4-84)$$

$$\rho v_2 \left. \frac{\partial \ln y_{\pm 2}}{\partial \rho_{o3}} \right|_{T, \rho_{o\gamma \neq 3}} = -v_2 v_3 c_{23}^o \quad (4-85)$$

Expressions involving salt 3 can be obtained from those in equations (4-81) to (4-83) by interchanging subscripts 2 and 3.

The preceding examples show that it is advantageous to write the thermodynamic properties in terms of salt-salt and salt-solvent functions, taking linear combinations of the ionic direct correlation function integrals. If we note that

$$x_i = \sum_{\alpha=1}^{n_o} x_{o\alpha} v_{i\alpha} \quad (4-86)$$

equations (4-44) through (4-46) can be transformed into these salt functions in the completely general case. We have

$$\frac{1}{\rho \kappa_T RT} = \sum_{\alpha=1}^{n_o} \sum_{\beta=1}^{n_o} v_{\alpha} v_{\beta} x_{o\alpha} x_{o\beta} (1 - c_{\alpha\beta}^o) \quad (4-87)$$

$$\frac{\bar{v}_{o\alpha}}{\kappa_T RT} = v_{\alpha} \sum_{\beta=1}^{n_o} v_{\beta} x_{o\beta} (1 - c_{\alpha\beta}^o) \quad (4-88)$$

$$\begin{aligned} \frac{1}{\rho \kappa_T RT} (\underline{G})_{\alpha\beta} = & v_{\alpha} v_{\beta} \sum_{\gamma=1}^{n_o} \sum_{\delta=1}^{n_o} v_{\gamma} v_{\delta} x_{o\gamma} x_{o\delta} [(1 - c_{\gamma\delta}^o)(1 - c_{\alpha\beta}^o) - \\ & (1 - c_{\alpha\gamma}^o)(1 - c_{\beta\delta}^o)] \end{aligned} \quad (4-89)$$

where

$$c_{\alpha\beta}^o \equiv \sum_{i=1}^n \sum_{j=1}^n v_{i\alpha} v_{j\beta} [1 - (\underline{C}^o)_{ij}] / v_{\alpha} v_{\beta} \quad (4-90)$$

and $v_{o\alpha} = 1$ if α is a solvent. Similarly, equation (4-50a) becomes

$$\rho v_{\alpha} \left. \frac{\partial \ln y_{\pm\alpha}}{\partial \rho_{o\beta}} \right|_{T, \rho_{o\gamma} \neq \beta} = - v_{\alpha} v_{\beta} c_{\alpha\beta}^o \quad (4-91)$$

Single-Solvent, Common Ion Case; Harned's Rule

The equations change somewhat when a two-salt system has a common ion, e.g., the anion, now denoted $-$. Then

$$c_{22}^o = [v_{2+}^2 (c^o)_{2+2+} + 2v_{2+}v_{2-} (c^o)_{2+-} + v_{2-}^2 (c^o)_{--}] / v_2^2 \quad (4-92)$$

$$c_{23}^o = [v_{2+}v_{3+} (c^o)_{2+3+} + v_{2+}v_{3-} (c^o)_{2+-} + v_{2-}v_{3+} (c^o)_{3+-} + v_{2-}v_{3-} (c^o)_{--}] \div v_2 v_3 \quad (4-93)$$

$$c_{33}^o = [v_{3+}^2 (c^o)_{3+3+} + 2v_{3+}v_{3-} (c^o)_{3+-} + v_{3-}^2 (c^o)_{--}] / v_3^2 \quad (4-94)$$

and the number of different direct correlation functions has been reduced from fifteen to ten. We choose the two positive ions as the dependent species.

The \underline{v} , \underline{y} and \underline{z} matrices for this system are

$$\underline{v} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & v_{2+} & 0 \\ 0 & 0 & v_{3+} \\ 0 & v_{2-} & v_{3-} \end{pmatrix} \quad \underline{y} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1/v_{2+} & 0 \\ 0 & 0 & 1/v_{3+} \\ 0 & 0 & 0 \end{pmatrix} \quad (4-95)$$

and

$$\underline{z} = \begin{pmatrix} 0 & -v_{2-}/v_{2+} & -v_{3-}/v_{3+} & 1 \end{pmatrix}^T \quad (4-96)$$

where again, multiplication by \underline{z}_- gives the vector of ionic charges.

Since the $C_{\alpha\beta}^0$'s use the \underline{v} matrix directly, whereas the $(\underline{H})_{ij}$'s must be transformed by \underline{z} , inverted, further transformed by combinations of \underline{X} , \underline{H} , \underline{z} , and \underline{y} , then inverted again, it is obvious that thermodynamic properties in terms of the direct correlation functions are much simpler mathematically.

Harned's rule for the mean ionic activity coefficients states that the logarithm of the mean ionic molal activity coefficient, γ_m , of one salt varies proportionally to the molality of the other salt when the total ionic strength, I , is kept constant. That is

$$\left. \frac{\partial \ln \gamma_{m\pm 2}}{\partial m_3} \right|_{T,P,I} = -\alpha_{23} \quad (4-97)$$

where $\gamma_{m\pm 2}$ and I are defined by

$$\mu_{o2}/kT = \nu_2 \ln [m_{\pm 2} \gamma_{m\pm 2}] + \mu_{o2}^0/kT \quad (4-98a)$$

$$I = (\nu_{2+} z_{2+}^2 + \nu_{2-} z_{2-}^2) m_2 + (\nu_{3+} z_{3+}^2 + \nu_{3-} z_{3-}^2) m_3, \quad (4-98b)$$

m_α is the molality of salt α and $m_{\pm 2}$ is the mean ionic molality of salt 2.

$$m_{\pm 2} = (m_{2+}^{\nu_{2+}} m_{2-}^{\nu_{2-}})^{1/\nu_2} \quad (4-99)$$

From the definitions of density- and molality-based activity coefficients in equations (4-48) and (4-98a), equation (4-97) can be rewritten

$$\left. \frac{\partial \ell n \gamma_{m \pm 2}}{\partial m_3} \right|_{T, P, I} = -\alpha_{23} = \sum_{\alpha=1}^3 \left. \frac{\partial \ell n \gamma_{\pm 2}}{\partial \rho_{o\alpha}} \right|_{T, \rho_{o\gamma} \neq \alpha} \left. \frac{\partial \rho_{o\alpha}}{\partial m_3} \right|_{T, P, I} + \left. \frac{\partial \ell n \rho_{\pm 2}}{\partial m_3} \right|_{T, P, I} - \left. \frac{\partial \ell n m_{\pm 2}}{\partial m_3} \right|_{T, P, I} \quad (4-100)$$

Next, we use equation (4-50) to write

$$\begin{aligned} \left. \frac{\partial \ell n \gamma_{m \pm 2}}{\partial m_3} \right|_{T, P, I} &= -C_{12}^o / \rho \left. \frac{\partial \rho_{o1}}{\partial m_3} \right|_{T, P, I} - v_2 C_{22}^o / \rho \left. \frac{\partial \rho_{o2}}{\partial m_3} \right|_{T, P, I} - v_3 C_{23}^o / \rho \left. \frac{\partial \rho_{o3}}{\partial m_3} \right|_{T, P, I} \\ &+ \frac{v_{2+}}{\rho_{o2}} \left. \frac{\partial \rho_{o2}}{\partial m_3} \right|_{T, P, I} + \frac{v_{2-}}{\rho_-} \left(\left. v_{2-} \frac{\partial \rho_{o2}}{\partial m_3} \right|_{T, P, I} + v_{3-} \left. \frac{\partial \rho_{o3}}{\partial m_3} \right|_{T, P, I} \right) \\ &- \frac{v_{2+}}{\rho_2} \left. \frac{\partial m_2}{\partial m_3} \right|_{T, P, I} - \frac{v_{2-}}{m_-} \left(v_{2-} \left. \frac{\partial m_2}{\partial m_3} \right|_{T, P, I} + v_{3-} \left. \frac{\partial m_3}{\partial m_3} \right|_{T, P, I} \right) \end{aligned} \quad (4-101)$$

The formulae for the necessary direct correlation function integrals can be obtained from Appendix I. They are

$$1 - C_{12}^o = \frac{\bar{v}_{o2}^\infty}{v_2 \kappa_1 RT} + \frac{3}{2} \frac{S_\gamma^1}{v_2 \kappa_1} \left. \frac{\partial \ell n \epsilon_1}{\partial P} \right|_T q_2 (x_{o2} q_2 + x_{o3} q_3)^{1/2} \rho^{1/2} + O(x_o) \quad (4-102)$$

$$1 - C_{23}^o = - \frac{S_\gamma^1 q_2 q_3 \rho^{1/2}}{2 v_2 v_3 (x_{o2} q_2 + x_{o3} q_3)^{1/2}} + B_{23} + O(x_o^{1/2}) \quad (4-103)$$

where $q_\alpha = v_{\alpha+} z_{\alpha+}^2 + v_{\alpha-} z_{\alpha-}^2$.

The expressions for $1-C_{22}^0$ can be obtained by replacing subscript 3 by 2 in equation (4-103), except in the term $(x_{o2}q_2 + x_{o3}q_3)$, where the 3 remains. The parameter $B_{\alpha\beta}$ will contain short range contributions from ions in salts α and β and long range terms in a universal form from the salts.

Equations (4-102) and (4-103) are substituted into (4-101) and considerable cancellation of terms occurs (including all terms proportional to the inverse of composition) leaving a series expression for the Harned coefficients, in terms of molality.

$$\begin{aligned} \alpha_{23} = \frac{M_1}{1000} & \left(v_2 \frac{q_3}{q_2} (B_{22}-1) - v_3 (B_{23}-1) - \frac{\bar{v}_{o2}^{\infty}}{v_2 \kappa_1 RT} \rho_1 \left(\frac{q_3}{q_2} \bar{v}_{o2}^{\infty} - \bar{v}_{o3}^{\infty} \right) \right) \\ & - v_2 \frac{M_1}{1000} \left(\frac{3}{2} \rho_1^{1/2} \frac{q_2}{v_2} \frac{s_1^1}{\kappa_1} \frac{\rho_1 M_1}{1000} \left(\frac{q_3}{q_2} \bar{v}_{o2}^{\infty} - \bar{v}_{o3}^{\infty} \right) \frac{\partial \ln \epsilon_1}{\partial p} \right) \Big|_T I^{1/2} + O(m) \end{aligned} \quad (4-104)$$

where M_1 is the molecular weight of the solvent (component 1). It is of interest to note that the Harned coefficient is a weak function of total ionic strength, which is constant for a given system, as well as of m_3 , which varies.

For a 1:1 electrolyte, the zeroth-order approximation to α_{23} is

$$\alpha_{23} = \frac{M_1}{1000} [B_{22} - B_{23} - \frac{\bar{v}_{o2}^{\infty}}{2\kappa_1 RT} \rho_1 (\bar{v}_{o2}^{\infty} - \bar{v}_{o3}^{\infty})] + O(I^{1/2}) \quad (4-105)$$

The values of B_{22} and B_{23} will have separate contributions from the ions and will depend only on temperature. Thus, in principle, α_{23} should be correlatable using only pure salt, pure solvent and infinite

dilution data. Conversely, the determination of Harned coefficients will aid in establishing expressions for the $(\underline{C}^0)_{ij}$.

CHAPTER 5 ELEMENTS OF A MODEL FOR ELECTROLYTIC SOLUTIONS

Introduction

The previous chapters give a formal basis for calculating system properties from direct correlation function integrals, but deal very little with precisely how these calculations can be performed or how these properties can be correlated or predicted using direct correlation functions. Previous work (Mathias and O'Connell, 1979, 1980a,b) has shown that properties for systems of non-"reactive" supercritical components dissolved in various solvents can be correlated and predicted quite well. In these systems, two pure-component parameters and one condition-independent binary parameter were sufficient for the accuracy desired. A more general result of this work is to indicate that the use of direct correlation function solution theory to model solution properties is most appropriate in systems where the components are very different from each other - hence the very good results for a mixture of supercritical and a subcritical component. This result stems from the mathematical form of the equations which amplify the effect of modeling errors when the values of the direct correlation function integrals are similar, and not from restrictions in the theory itself. With this knowledge and the work of the previous chapters in mind, solutions of electrolytes seem to be a natural application of

this theory, due to the "reactive" nature of the electrolytic dissociations and the differences in the physical nature of the solvents and ions.

This chapter concerns the basis and general formulation of a simple model for electrolytes, and how this model can be used, e.g. in determining activities of electrolytes or the effect of salts on vapor liquid equilibria. The model is not complete, but a few preliminary results are given.

The Primitive Ion Model

The primitive ion model approximates an ion in solution as a hard sphere with an electric charge at its center. Thus, an ion i is completely described by charge parameter z_i (number of elementary charges) and a size parameter σ_i (hard sphere diameter). There are a number of theories based on this view of an ion. The simplest is the Debye-Hueckel Theory, which looks at one ion in a uniform field generated by all the remaining ions, and in its original form considers the ion's diameter to be zero. This theory gives exact results for very dilute solutions (e.g. 10^{-4} molar aqueous solutions for ions with single charges). A more recent approximation to a solution of primitive ions is known as the Mean Spherical Model (Lebowitz and Percus, 1966). It has been solved for both the "restricted" case, where all ions have equal sizes and charges (Waisman and Lebowitz, 1970), and in the general case of arbitrary sizes and charges (Blum, 1975). Unfortunately, this model requires tedious iterative calculations in all but the restricted case, and does not give the correct results in the limit as the salt concentration goes to zero (i.e. Debye-Hueckel

results). This model gives good results for solutions of moderate concentrations in both the general and restricted cases (Grigera and Blum, 1976; Triolo et al., 1976).

The model proposed here, also using the primitive ion basis, is easier to use than the Mean Spherical Model, but should give reasonable accuracy in moderately concentrated solutions of electrolytes, as well as go to the Debye-Hueckel limits as the salt concentration vanishes. Work by Long and McDevit (1952), Shoor and Gubbins (1969) and Lucas (1969) indicate that the major portion of the activities of mixtures of solvents and electrolytes stems from the volumetric, or size, effects of the individual components, rather than the electrostatic effects. For this reason, we choose to model the direct correlation function integral as the sum of a hard-sphere term plus a deviation, or perturbation, which will largely be from the Debye-Hueckel theory. This parallels the approach of Mathias and O'Connell (1979), where the perturbation to the hard-sphere integral was a second virial coefficient term. We use

$$C_{ij} = \rho \int c_{ij}(\underline{r}) d\underline{r} = \rho \int c_{ij}^{hs}(\underline{r}) d\underline{r} + \rho \int [c_{ij}(\underline{r}) - c_{ij}^{hs}(\underline{r})] d\underline{r} \quad (5-1)$$

where the hard-sphere term can be obtained from differentiation of the mixture form of the Carnahan-Starling equation of state for hard-spheres (Mansoori et al., 1971). The hard-sphere portions of the direct correlation function integrals and activity coefficients are given in Appendix I. The perturbation term comes from the electrostatic contributions and includes the Debye-Hueckel limits given in equations (4-69) through (4-70), as well as terms from the Mean Spherical Model.

Calculation of Solution Properties

Before the model for these direct correlation function integrals is examined in more detail, it is important to understand the process used in carrying out an actual calculation. The C_{ij}^0 's are written as functions of T and $\underline{\rho}$ and, as shown in equations (4-40) through (4-50), are related to the following density derivatives of thermodynamic properties:

$$\left. \frac{\partial P/RT}{\partial \rho_{o\alpha}} \right|_{T, \rho_{o\gamma \neq \alpha}} = \sum_{i=1}^n v_{i\alpha} \sum_{j=1}^n \frac{\rho_i}{\rho_o} [1 - (\underline{C}^0)_{ij}] \quad (5-2a)$$

and

$$\left. \frac{\partial \ell_{ny_{o\alpha}}}{\partial \rho_{o\beta}} \right|_{T, \rho_{o\gamma \neq \beta}} = - C_{\alpha\beta}^0 / \rho_o \quad (5-2b)$$

In a typical problem, the activity coefficients of the components of a solution are desired at a particular state -- usually defined by the variables T^f , P^f and \underline{x}_o^f . Since the $(\underline{C}^0)_{ij}$'s are related to derivatives of the quantities of interest, it is obvious that we need to know the complete set of activity coefficients at some reference state given by T^r , P^r and \underline{x}_o^r . (Actually, values of the activity coefficients at reference conditions are needed only for those components whose activity coefficients are to be calculated at T^f , P^f and \underline{x}_o^f). Furthermore, since equations (5-2) give only density derivatives, the reference state temperature must equal the final temperature ($T^r = T^f$), and the reference state density must be known (ρ^r).

The simplest procedure for the calculation is to make a guess of the density at the final state $(T^f, P^f, \rho^f, \underline{x}_0^f)$, noting that the component densities, the $\rho_{o\alpha}$'s, are given by $\rho_{o\alpha} = x_{o\alpha}\rho$. Then equation (5-2a) is integrated successively for each component (i.e. from state $\{T^r, \rho_{o1}^r, \rho_{o2}^r, \dots\}$ to state $\{T^r, \rho_{o1}, \rho_{o2}, \dots\}$ to state $\{T^r, \rho_{o1}, \rho_{o2}, \dots\}$ and so forth). This gives a pressure P' which corresponds to the desired mole fractions, but probably incorrect total density. We then use equation (4-44), which can be rewritten

$$\left. \frac{\partial P/RT}{\partial \rho} \right|_{T, \underline{N}} = \sum_{\alpha} \sum_{\beta} x_{o\alpha} x'_{o\beta} (1 - C_{\alpha\beta}^o) \quad (5-3)$$

Equation (5-3) is integrated to give

$$\frac{P^f - P'}{RT} = \sum_{\alpha} \sum_{\beta} x_{o\alpha} x_{o\beta} \left[1 - \int_{\rho}^{\rho^f} C_{\alpha\beta}^o(\beta, x_{oj}^T) d\rho \right] \quad (5-4)$$

Integration of equation (5-2a) can be performed analytically or numerically - in either case it is a simple quadrature. The integration in equation (5-4) can also be done either numerically or analytically. If done numerically, simple quadrature is performed until the value of the right hand side equals the known value of the left hand side, the end point of the integration interval being ρ^f , the desired quantity. If done analytically, a root finding procedure for ρ^f must be employed. Because these are simple integrations rather than solutions to differential equations, they can be done quickly and efficiently on a computer.

Once ρ^f is known, equation (5-2b) can be integrated using the same procedure as followed with equation (5-2a), except that now the final limit is known with certainty and further integration at constant composition is unnecessary. These integrations can also be performed either numerically or analytically (see Appendix J for integrated form of equation 5-2b).

The flexibility that this process has due to the use of a reference state should not be overlooked. For a system of salts in a single solvent, the use of the pure solvent as the reference state, and correspondingly, considering infinite dilution to be the reference state of the salts, only the solvent density at an arbitrary reference pressure (the temperature must, of course, be the same as the final temperature) is needed for reference data. A more important example of judicial selection of the reference state occurs in vapor-liquid equilibria calculations. Assuming we have one salt in some liquid mixture, the salt-free mixture with the same mole ratios of non-electrolyte components can be viewed as a single pseudo-component, and this solvent used as the reference state. From experiments, or theories of non-electrolyte solutions, the values of ρ^r and the non-electrolyte activity coefficients can be obtained. This procedure allows for interactions between the solvent constituents to be taken into account by more accurate models. Finally, the integration of equations (5-2) need only be performed over the salt number density and solvent "pseudo-component" density, rather than the entire set of densities. This procedure allows the salt-effects on the solution properties to be determined using our model, but does not restrict the solvent-solvent interactions to the primitive ion restrictions.

Thus, the heavy dependence on a reference state has several effects, both positive and negative. It requires accurate density and activity data at the reference state, but allows us to make use of any available data that might minimize the length of the integration path. And, it allows us to be concerned only with the effects of the electrolytes and total density, and so make use of other methods which might be more appropriate for the solvents of interest when accounting for solvent-solvent interactions.

Electrostatic Contributions to the Direct Correlation Function Integrals

Since the largest contribution to the effect of ions in solution properties is the effect of the ion size, accounted for by the hard sphere portion of the direct correlation function integral, the electrostatic contributions can be included in an approximate way without a great loss in accuracy. Therefore, the superposition of the Debye-Hueckel limits on the hard sphere relation is considered adequate for the electrostatic effects on solvent-solvent and a valid approximation for ion-ion interactions. Mathematically speaking, the Debye-Hueckel limits can be looked at as truncations of half-power expansions in salt density, with the largest exponents being three-halves, one-half and negative one-half respectively for solvent-solvent, solvent-ion and ion-ion interactions (equations I-4a through I-4b). Since the largest effect is formed in ion-ion interactions, it is necessary to extend that series to higher powers of the salt density. It is here that some results from the Mean Spherical Model are used.

Beginning with the general solution of the Mean Spherical Model (Blum, 1975) and approximately expanding in half-powers of the salt density gives indications that the electrostatic contribution to the direct correlation function integrals can be written

$$-C_{ij}^{\text{elec}} = z_i^2 z_j^2 \sum_{k=0}^{\infty} D_{ijk}(\underline{\sigma}, \underline{\eta}) \kappa^k \left(\frac{\rho \alpha}{\kappa} \right)^4 \quad (5-5)$$

with the following definitions of the terms on the right hand side:

z_i = charge (in units of elementary charge) on ion i ,

$\alpha^2 = \frac{4\pi e^2}{\epsilon_o kT}$ and has units of length,

$\kappa = \alpha^2 \sum_j \rho_j z_j^2$ = inverse debye length,

σ_i = radius of ion i ,

η_k = a weighted average of ion sizes, having units of $(\text{length})^k$ and defined by

$$\eta_k = \frac{\sum_j \rho_j z_j^2 \sigma_j^k}{\sum_i \rho_i z_i^2} \quad (5-6)$$

It is important to note that if we factor out the total ionic density $(\sum_{\text{ions}} \rho_i)$ from both numerator and denominator of the η_k 's, they are seen to be functions of the ratios of the salt mole fractions among themselves. That is, if the salts in a solution are held in constant

proportion to each other, the η_k 's remain unchanged if the total salt density is changed. Thus $\underline{\eta}$ is not a function of the total salt concentration, only the relative concentrations.

Finally, we must define the functions $D_{ijk}(\underline{\sigma}, \underline{\eta})$. A general form for these functions has not been determined, but the dependence on $\underline{\sigma}$ and $\underline{\eta}$ has been determined for k values ranging from zero to four.

These are

$$D_0 = a_0$$

$$D_1 = a_1(\sigma_i + \sigma_j)$$

$$D_2 = a_2\{\eta_1(\sigma_i + \sigma_j) + 2\sigma_i\sigma_j - \frac{1}{4}\eta_1^2\} + b_2\{\sigma_i^2 + \sigma_j^2 + \frac{1}{2}\eta_2\}$$

$$D_3 = a_3\{\eta_1\sigma_i\sigma_j\} + b_3\{(\sigma_i\sigma_j + \eta_2)(\sigma_i + \sigma_j) + \eta_1(\sigma_i^2 + \sigma_j^2)\}$$

$$+ c_3(\sigma_i^3 + \sigma_j^3 + \eta_3)$$

$$D_4 = a_4\{6\sigma_i\sigma_j - \eta_1(\sigma_i + \sigma_j) - 3/8\eta_1^2\}\eta_1^2$$

$$+ b_4\{2\sigma_i\sigma_j\eta_2 + (2\sigma_i\sigma_j + \eta_2)(\sigma_i + \sigma_j)\eta_1$$

$$+ \frac{1}{2}\eta_1^2(\sigma_i^2 + \sigma_j^2) - \frac{1}{4}\eta_1^2\eta_2\}$$

$$\begin{aligned}
& + c_4 \{ 3/2 \eta_1 (\sigma_i^3 + \sigma_j^3) + \sigma_i \sigma_j (\sigma_i^2 + \sigma_j^2) + 3/2 \eta_3 (\sigma_i + \sigma_j) + 3/4 \eta_1 \eta_3 \} \\
& + d_4 \{ 2 \sigma_i^2 \sigma_j^2 + 3 \eta_2 (\sigma_i^2 + \sigma_j^2) + 3/4 \eta_2^2 \} + e_4 \{ \sigma_i^4 + \sigma_j^4 + 3/2 \eta_4 \}
\end{aligned}$$

In the above equations, the a_i 's, b_i 's, c_i 's, d_4 and e_4 are pure numbers arising from multinomial and binomial expansion coefficients, and are very complex. The Mean Spherical Model is only an approximation to the ions' behavior, and in fact gives an incorrect result at infinite dilution. Furthermore, this truncated expansion is only an approximation to the low density (<1 Normal) limit of this model. So rather than evaluating these constants, we consider them to be universal parameters to be fitted from data. Furthermore, in the $k=0$ term (which is proportional to salt density to the minus one-half power), a_0 is replaced by the correct Debye-Hueckel limit of equation (I-4c).

The Form of the Complete Model

The individual contributions to the model for the direct correlation function integrals have been defined in the preceding sections and Appendices I and J. Now these parts must be combined to form the total model. We consider a system of a mixed solvent pseudo-component denoted by the subscript s , and n_s salts denoted by the subscripts α and β , where α, β range from 1 to n_s . The general equations for the $C_{\alpha\beta}^0$'s are then

$$\begin{aligned}
1 - C_{ss}^o &= 1 - C_{ss}^{hs} - (1 - C_{ss}^{hso} - C_{ss}^{hs'} + \frac{\phi_K^o}{\kappa_s^2 RT}) \sum_{\gamma} v_{\gamma} x_{o\gamma} \\
&+ \left(\frac{S_V^1}{\kappa_s RT} + \frac{S_Y^1}{2} + \frac{3}{2} \frac{S_K^1}{\kappa_s RT} \right) \left(\sum_{\gamma} x_{o\gamma} q_{\gamma} \right)^{3/2} \rho^{1/2} \quad (5-7a)
\end{aligned}$$

$$\begin{aligned}
1 - C_{s\alpha}^o &= \frac{1}{v_{\alpha}} \sum_i v_{i\alpha} (1 - C_{is}^{hs}) + \frac{\bar{v}_{o\alpha}^{\infty}}{v_{\alpha} \kappa_s RT} - \frac{1}{v_{\alpha}} \sum_i v_{i\alpha} (1 - C_{is}^{hso}) \\
&+ \frac{3}{2} \frac{S_Y^1}{v_{\alpha} \kappa_s} \left. \frac{\partial \ln \epsilon_s}{\partial \rho} \right|_T q_{\alpha} \left(\sum_{\gamma} x_{o\gamma} q_{\gamma} \right)^{1/2} \rho^{1/2} \quad (5-7b)
\end{aligned}$$

$$\begin{aligned}
1 - C_{\alpha\beta}^o &= \frac{1}{v_{\alpha} v_{\beta}} \sum_{\alpha} \sum_{\beta} v_{i\alpha} v_{i\beta} (1 - C_{ij}^{hs}) - \frac{S_Y^1 q_{\alpha} q_{\beta} \rho^{1/2}}{2 v_{\alpha} v_{\beta} \sum_{\gamma} (x_{o\gamma} q_{\gamma})^{1/2}} \\
&+ \alpha^4 \rho \sum_{\alpha} \sum_{\beta} v_{i\alpha} v_{j\beta} z_i^2 z_j^2 \sum_{k=1}^{\infty} D_{ijk} \kappa^{k-1} \quad (5-7c)
\end{aligned}$$

In these equations κ_s and ϵ_s are the isothermal compressibility and dielectric constant of the mixed solvent (salt free). The other variables are defined in the sections dealing with the specific portions of the direct correlation function integrals. The superscripts hs, hso, hs, and hsl are hard sphere contributions and are given in Appendix J.

Preliminary Results

Although fitting of the parameters in the D_{ijk} 's is beyond the scope of this work, some preliminary, approximate calculations were made for the sodium chloride-water system. These calculations were carried out by fitting the three direct correlation function integrals

(water-water, water-salt, and salt-salt) to compression data from Gibson and Loeffler (1948) and the activity data reported by Robinson and Stokes (1965). Then with the dielectric constant and its derivatives taken from the data of Owen et al. (1961), the water-water and water-salt integrals were recalculated according to equations (5-7). Using the known final density [instead of using equations (5-2a) and (5-4)] and infinite dilution partial molar volumes of the ions, and the above $C_{\alpha\beta}^0$ values, the thermodynamic properties of the solution were calculated. The results are given in Table 1 along with the σ_i values.

This procedure gives calculated values of reduced compressibility within five per cent error, reduced partial molar volumes within nine per cent (one per cent for NaCl) and derivatives of the activity coefficient within twenty per cent at concentrations as high as five to six molar. The errors are systematic, and may be correctable without too much difficulty. For example, although using the above procedure to integrate (5-2a) or (5-4) may lead to inaccurate densities; it may lead to more accurate activities than is implied here because consistent application of the model will have been made. Further refinements to the model, as well as correlation of the higher terms in the ion-ion direct correlation function should lessen these errors.

As hoped, this modeling procedure is a viable method for correlating and predicting properties of salt solutions. Further refinements are needed, of course, yet this beginning appears to be quite promising. Further work on improving the accuracy is presently being undertaken.

TABLE 1
COMPARISON OF EXPERIMENTAL AND CALCULATED PROPERTIES OF ELECTROLYTES

m	$\nu_{2^xO_2}$	$\nu \frac{cm^3}{gmol}$	$\frac{1}{\rho \kappa_T RT}$		$\frac{\bar{\nu}_2}{\kappa_T RT}$		$\frac{\nu N}{\rho \kappa_T RT} \frac{\partial \ln \gamma_{\pm}}{\partial N_{O_2}} \Big _{T,P,N_{O_1}}$	
			exp	calc	exp	calc	exp	calc
NaCl @ 25°C	0	18.069	15.96	15.96	14.57	14.57	-34.96	-34.96
	1.94	17.517	18.96	20.07	22.43	22.38	61.50	50.12
	4.27	17.036	22.30	23.97	29.68	29.57	159.79	129.32
	5.68	16.801	24.13	26.10	33.65	34.11	211.33	178.36
NaBr @ 25°C	0	18.069	15.96	15.96	20.89	20.90	-34.96	-34.96
	1.70	18.300	18.50	19.15	27.85	29.08	62.94	53.84
	5.13	18.842	23.30	24.42	38.68	41.46	190.23	154.72

The hard sphere diameters used are:

$$\begin{aligned} \sigma_w &= 2.73 \text{ \AA} & \sigma_{Cl^-} &= 3.90 \text{ \AA} \\ \sigma_{Na^+} &= 1.90 \text{ \AA} & \sigma_{Br^-} &= 4.05 \text{ \AA} \end{aligned}$$

CHAPTER 6
AN EXPERIMENT FOR VOLUMETRIC PROPERTIES OF SALT SOLUTIONS
AT HIGH PRESSURES

Introduction

A molecule in a solution, held at a constant temperature and composition, would notice changes in the pressure of the solution, not so much by the force exerted on the boundary of the solution, as by the nearness of other molecules in the solution. This concept leads to the notion that when looking at solutions in terms of their intermolecular interactions, the density becomes the fundamental variable, and the pressure a measured, or perhaps, derived property. It is the fact that the density is a more direct measurement of the interactions between molecules, that it is of great interest to look at the variation of thermodynamic properties along isochoric, rather than isobaric, surfaces in P - V - T - \underline{x} space. Further motivation is given by calculations by O'Connell (1980) from experimental data by Gibson and Loeffler (1948). There it is shown that the mole fraction derivative of the salt activity coefficient of sodium chloride in water is a much smoother and weaker function of composition along isochores than along isobars.

The purpose of high pressure volumetric measurements of salt solutions is to be able to look at activities and activity coefficients of the components of such solutions on these surfaces of constant density, the elevated pressures being necessary because of the relative insensitivity of density to pressure as compared to its sensitivity to

composition and temperature. For example, water at 1 atm and 25°C has a coefficient of thermal expansivity of $2.57 \times 10^{-4} \text{ } ^\circ\text{K}^{-1}$, and a coefficient of isothermal compressibility of $4.52 \times 10^{-5} \text{ bar}^{-1}$. These values correspond to a pressure increase of approximately 5.7 bar for every one degree increase in temperature along the line of constant density in the P-T plane. Because of similarly strong composition effects on density (especially at lower salt concentrations), one can see that a large pressure range is required if a reasonable temperature and composition range is used.

This chapter deals with the use of the P-V-T-x data to calculate activities and activity coefficients, as well as the operation and design of the apparatus itself. Since the apparatus is that of Grindley and Lind (1971) and Grindley (1971) with only minor changes, the dimensions, details of calibrations and equipment specifications are left to those references. Only a more general description, including alterations, is given here.

Thermodynamic Basis

Given that data from this experiment is available over a spectrum of P-V-T-x values for the solution of interest, we now look at the calculation of the activities and activity coefficients on a constant density surface. The variation of activity with temperature and composition cannot be derived from P-V-T-x data alone, but the variation with respect to P at constant T and x is given by

$$\left. \frac{\partial \ln \hat{a}_{o\alpha}}{\partial P} \right|_{T, \underline{x}} = [\bar{v}_{o\alpha}(T, P, \underline{x}) - \bar{v}_{o\alpha}(T^0, P^0, \underline{x}^0)]/RT \quad (6-1)$$

where the superscript zero refers to the reference state used for the activity. Equation (6-1) can also be used for the activity coefficient by replacing $\hat{a}_{o\alpha}$ with $\gamma_{o\alpha}$.

The partial molar volume, $\bar{v}_{o\alpha}$, can be calculated by fitting the P-V-T- \underline{x} data and differentiating. For data in this form, the equation

$$\bar{v}_{o\alpha} = v - \sum_{\beta \neq \alpha} x_{o\beta} \left(\frac{\partial v}{\partial x_{o\beta}} \right)_{T, P, x_{o\gamma \neq \beta, \alpha}} \quad (6-2)$$

is the most direct. Once all the mole fraction derivatives are determined, all the partial molar volumes can be easily calculated. Similarly, the partial molar volume at the standard state is determined using equation (6-2) with data from around the standard state.

Of course, the P-V-T- \underline{x} data only gives the changes in activity as the pressure changes. So, we need to know the activity of the components in a solution at the temperature and composition of interest and some other pressure. Also, we need to supplement our measurements with published values of activities at normal pressures, which are readily available for many systems. Having the activity of component α at T, P', \underline{x} , where P' is the pressure from the outside reference, we can calculate $\ln \hat{a}_{o\alpha}$ at any pressure using the relation

$$\ln \hat{a}_{o\alpha}(T, P, \underline{x}) = \ln \hat{a}_{o\alpha}(T, P', \underline{x}) + \frac{1}{RT} \int_{P'}^P (\bar{v}_{o\alpha} - \bar{v}_{o\alpha}^o) dP \quad (6-3)$$

as long as the $\bar{v}_{o\alpha}$'s are available at T and \underline{x} over the complete pressure range from P' to P . If the standard state for the activity is a fixed pressure P^o and not the system pressure (which varies from P' to P), we may rewrite equation (6-3) as

$$\ln \hat{a}_{o\alpha}(T, P, \underline{x}) - \ln \hat{a}_{o\alpha}(T, P', \underline{x}) = \frac{\bar{v}_{o\alpha}^o}{RT} (P - P') + \frac{1}{RT} \int_{P'}^P \bar{v}_{o\alpha} dP$$

Equations (6-1) through (6-3) enable the activities to be calculated over the entire range of P-V-T- \underline{x} data, assuming that they are available at some pressure for the same T- \underline{x} range. Since the volumes are measured throughout the range of P-T- \underline{x} , the isochoric surfaces can be constructed for the activity in the space of the variables T and \underline{x} .

Experimental Design

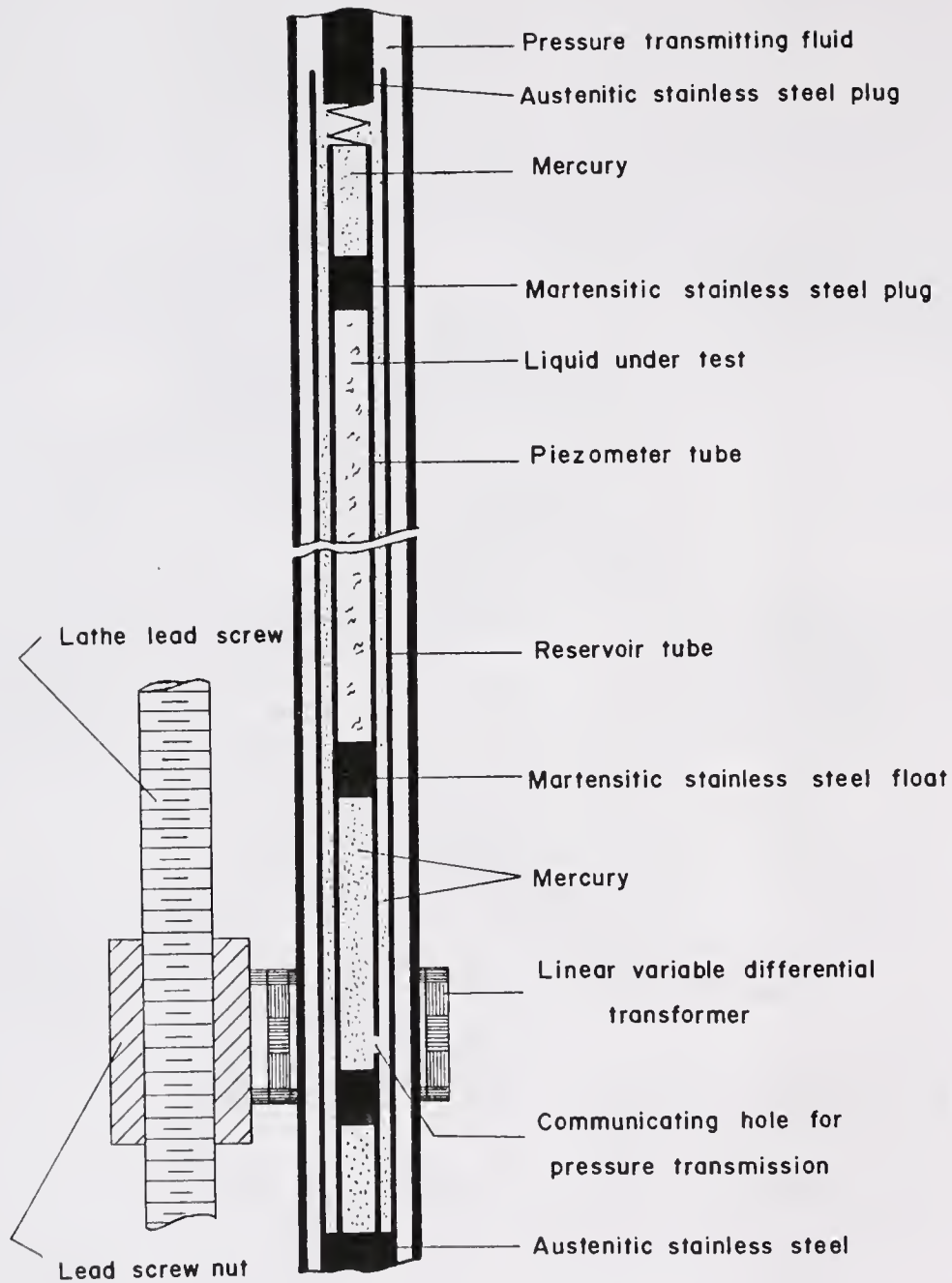
The apparatus used consists of two major components. One is the piezometer apparatus, including a pressure tube, piezometer tube, and volume measuring devices contained in a constant temperature bath. The other is the pressure plant, including pressure generating and measuring devices. The main portions of these components are sketched in Figures 6 and 7 respectively. These figures are described in the following sections.

Piezometer Design

The piezometer tube itself is a non-magnetic (austenitic) stainless steel tube which holds the sample. One end of the tube is sealed with a magnetic (martensitic) stainless steel plug. The other end has an identical plug, but it is removable. This allows a snugly fitting martensitic stainless steel float to be placed against the test liquid, and for the remainder of the tube to be filled with mercury. When the plug is in position, a small hole in the piezometer tube wall allows pressure to be transmitted to the mercury inside the tube, and hence to the sample itself. The mercury acts as a seal to prevent any leakage around the float. The piezometer tube fits inside a mercury reservoir tube, and then the entire assembly slides into the pressure tube. Here the mercury contacts the oil which is the pressure transmitting fluid in the pressure plant. This configuration is shown in Figure 6.

The pressure tube is fixed to a bracket which also holds the mechanical portion of the volume measuring apparatus. This portion consists of a linear variable differential transformer (LVDT) which is attached to a motor-driven, lathe lead screw. The LVDT detects the location of the upper plug and the float in the piezometer tube. The lathe lead screw then allows the position of the LVDT to be known very accurately. A counter attached to the motor drive is used to count rotations of the lead screw, which can be converted into the length of the sample liquid columns in the piezometer tube.

The LVDT is simply three coils, the primary coil through which an AC signal is sent, and two identical secondary coils which are arranged symmetrically around the primary coil. The secondary coils



PIEZOMETER APPARATUS

Figure 6. Piezometer apparatus for volume determinations.

are wired such that the total voltage across the two coils is zero when the martensitic stainless steel plug or float is centered between the secondary coils. By adjusting the lead screw, the output from the LVDT can be nulled, which corresponds to locating the desired position. The difference between the location of the plug and that of the float gives the length of the liquid column.

Pressure Plant

Pressure is generated in the apparatus by operation of a hydraulic hand pump connected to the low pressure side of a pressure intensifier. The intensifier's high pressure side is connected to the piezometer apparatus, where pressures in excess of 8000 bar can be attained. Another hand pump, the reversing pump, is used to return the pressure transmitting piston of the intensifier to its initial position after the pressurization is completed. A valve with its valve seat drilled out is used for fine pressure adjustments. For pressure measurements, the pressure plant includes a 300 bar Heise gauge and 40,000 psia Heise gauge which are used for low and intermediate pressures, respectively. Intermediate and high pressures are determined using a manganin gauge which is described in the following paragraph. A schematic of the entire pressure plant is given in Figure 7.

The manganin gauge measures pressure by measuring the change in resistance of a non-inductively wound coil of manganin alloy. The pressure response of this alloy is extremely linear, and can be calibrated using a dead weight gauge for the low pressure range (where non-linearity is highest) and the freezing pressure of Mercury at 0°C,

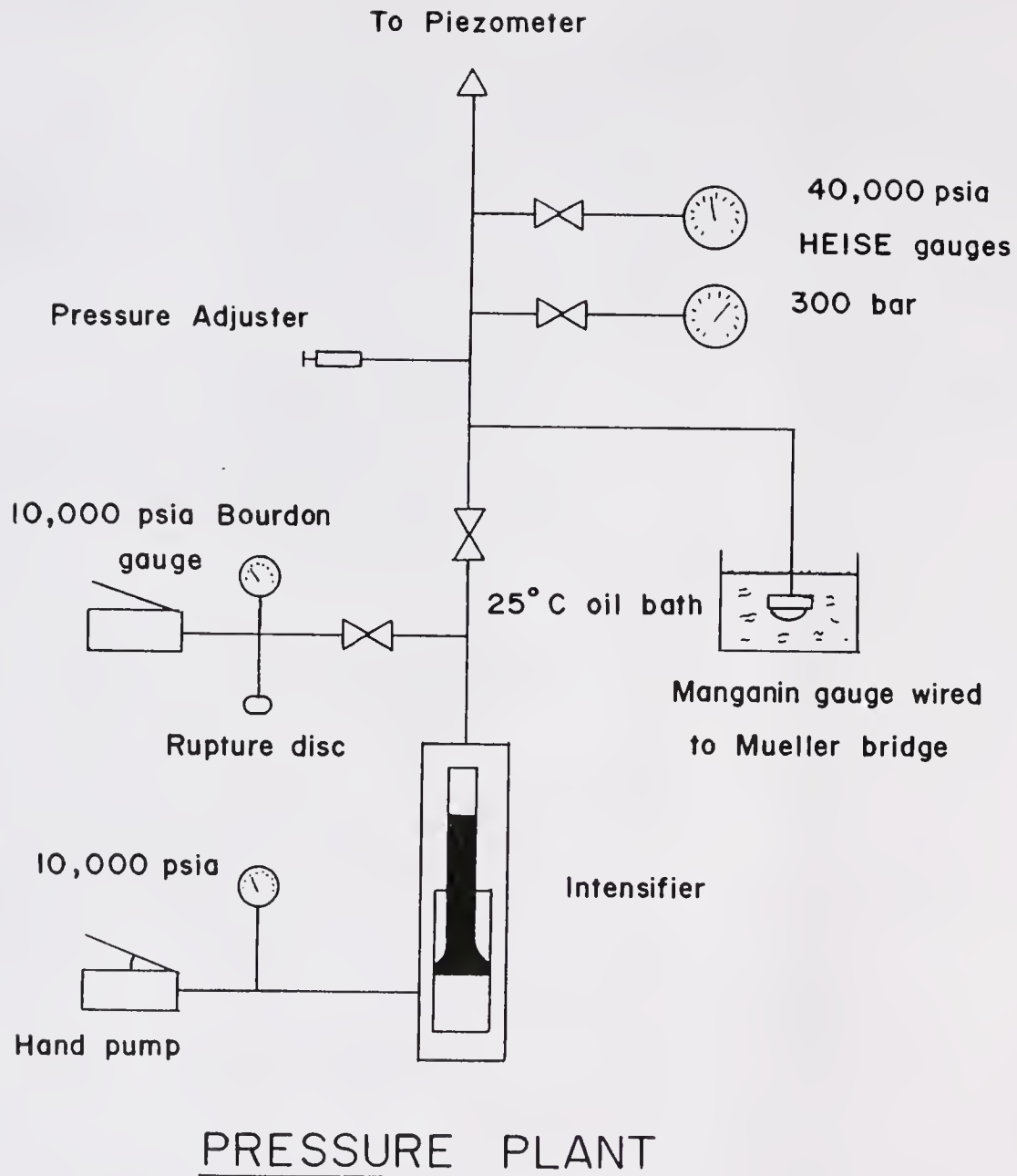


Figure 7. Pressure plant for experimental apparatus. .

which is 7569 bars, to fix the slope in the linear region. The gauge itself consists of two identical coils, one at system pressure and one at ambient pressure, set in a constant temperature bath. These coils are connected to a Mueller bridge and the resistance is determined by balancing the circuit using a decade box. Again, the details can be found in Grindley (1971).

Unfortunately, defects in the decade box have caused the manganin gauge to be temporarily abandoned, and replaced with a Ruska dead weight gauge. This limits the pressure range to 12000 psia (about 800 bar). For future work, the decade box will be replaced with a newer design and the manganin gauge will again be operational.

Operating Procedures

As in the previous section, the operating procedure contains little new material and can be found in detail in Grindley and Lind (1971) and Grindley (1971). Only the change to the use of the dead weight gauge will be given in detail.

Calibration and Correction of Raw Data

All of the compression and thermal expansion coefficients for the various materials are readily available in the references, but the following factors cause the raw data to need correction:

- Thermal expansion of lead screw, causing the measured column length to be too short at higher temperatures.
- Linear compression of martensitic plugs and floats, causing the liquid to have more volume between the centers of these pieces.

- *Radial compression of the piezometer tube walls, causing the cross sectional area of the fluid column to increase as pressure increases.

- *Difference in pressure at the pressure measuring point and the piezometer tube caused by the height of the mercury transmitting fluid.

Other factors influencing the measurements are automatically accounted for (e.g. low pressure non-linearity of manganin gauge, and temperature compensation of the Heise pressure gauges--which is built into the gauges themselves) or are negligible (e.g. variation in bath temperature both in the piezometer bath and the manganin gauge bath, pressure effect of oil column).

Actual calibration of the system can be obtained by taking measurements on pure water and comparing it to available data. This will also lead to an accurate estimation of the accuracy of the volume measurements.

Piezometer Preparation

The first step in the preparation of the piezometer apparatus is the placement of the sample into the piezometer tube. The end of the tube with the removeable plug is pointed upward, the plug removed, and the liquid slowly injected into the tube using a syringe, being careful not to entrap any gas in the tube. The float is then inserted and the tube filled with mercury, again using a syringe. Reinsertion of the plug follows, and mercury should flow out of the pressure transmitting hole. Additional mercury (about 1.5c) is placed in the reservoir tube, and the piezometer tube is carefully inverted and slid into this

tube. The entire assembly is now placed into the pressure tube, taking care to push the reservoir tube as far into the pressure tube as possible. The pressure tube is now filled with oil and the tubing connections to the pressure plant reassembled.

Pressure Generation and Measurement

The sample is pressurized by operation of the main hand pump with the valve to the reversing pump closed. Pumping is continued until the pressure shown on the Heise gauge is approximately the desired pressure (for pressures below 300 bar). The pressure can be adjusted more finely using the pressuring adjusting valve. For higher pressures, two changes must be made. Firstly, the pressure must be generated in two steps, and secondly, the final pressure must be measured with the man-ganin gauge (the procedure for the dead-weight gauge is given later).

At a pressure of about 400 to 450 bar, the piston of the pressure intensifier reaches its limit of motion. At this point, the valve connecting the intensifier to the rest of the high pressure apparatus is closed and the valve to the reversing pump is opened. The valve to the oil reservoir for the main hand pump is opened as well. The reversing pump is then used until the piston has returned to its initial position in the intensifier, and the pressure at the reversing pump is approximately that of the isolated system. The reversing pump valve is closed, the oil reservoir valve opened, and then the valve connecting the intensifier to the piezometer apparatus is opened very slowly to reduce the possibility of damage caused by a pressure differential across this valve. The system can continue to be pressurized as before.

Since the highest range on the Heise gauges ends at 40,000 psig, the manganin gauge must now be relied on totally for pressure measurements. This is best accomplished by setting the decade box to the setting which corresponds to the desired pressure, and adjusting the null detector to a low sensitivity. As the null meter shows this pressure being approached, the sensitivity is increased until fine adjustment is to be made, where highest sensitivity must be used. When the meter is nulled for a few seconds, the pressure tube valve should be closed to reduce the chance of leakage, and the volume measurements can be taken.

When the Ruska dead-weight gauge is used instead of the manganin gauge, a different procedure is used. In this case the desired weight is placed on the gauge, and the system pressurized until the weights are lifted well above the reference line on the gauge. The weights are allowed to settle (due to slow leaking around piston in dead weight gauge) and the pressure tube valve is closed when the weights cross the reference plane. This gives the desired pressure in the piezometer apparatus.

Temperature Measurement and Control

The temperature of the system is controlled by the bath in which the piezometer apparatus is situated. This bath utilizes a silicon oil which has a very low vapor pressure, even at 150°C. The temperature is controlled using a standard proportional controller, and measured using a Hewlett-Packard digital thermometer. The bath is stirred and temperatures vary less than .02°C with position in the

vicinity of the pressure tube. Temperature changes can be accomplished quickly using two hairpin heaters designed for that purpose. Because temperature equilibrium is established slowly, the entire spectrum of pressures is measured at a given temperature, before the temperature is changed. Since taking measurements for the entire pressure range is a day-long procedure, the temperature can be changed and allowed to equilibrate overnight. In any case, at least one hour should be allowed for the piezometer apparatus to come to equilibrium with the bath.

Volume Determination

The crux of this experiment is, of course, determining the density, or volume, of the sample. The two important determinations are the length of the liquid column and the size of the sample. The composition of the sample is determined when the sample is made up; however, the weight, or number of moles of sample used is not directly determined. This is because some solution may flow past the float during the filling procedure, before the mercury can seal the interface. The mercury then displaces this liquid, which spills out along with some mercury when the plug is reinserted. The sample size then must be determined by comparison of low pressure measurements taken in this apparatus, to any available low-pressure data. For pressures around one atmosphere, this presents little difficulty.

When the desired temperature and pressure have been attained inside the piezometer, the LVDT is used to measure the distance between the upper plug and the float of the piezometer tube. The motor switch is turned on and the voltmeter watched for the presence of the

magnet in the field of the LVDT. When the magnets are far from the coils, there is zero voltage. In the vicinity of a magnet, the voltage jumps suddenly, then returns to zero when the magnet is centered in the coil. As the magnet is passed, the voltage slowly increases and then drops sharply after the magnet passes completely out of the coil. The reading on the turn counter for the motor is taken for the upper plug and the float, and is converted into distance using the gear ratio from the motor to the lathe lead screw, and the screw pitch (corrected for temperature). The tube diameter is known, and after it is connected for pressure effects, can be multiplied by the column height to give the volume of the solution. (The measured length must also be connected for the size of the magnets, since it locates their centers). Since the size of the sample can be determined, the molar volume and density can be readily calculated.

Conclusions

Although the experiment has been operated, no real data has been taken, or will be taken by the author. Only the construction and preparation of the apparatus, not actual measurements, are within the scope of this work.

CHAPTER 7 CONCLUSIONS

This work has focused on the application of these general principles to solution thermodynamics of "reactive" systems --that is, the description of solutions of "reactive" components in a consistent manner, using both theoretical and empirical considerations. First, the requirements of a consistent model, as developed from classical thermodynamics have been formulated, both in the form of a test, and in the form of a procedure, based on spatial projections, which builds this interval consistency into the model development.

Using this general procedure, the solution theory of Kirkwood and Buff (1951) has been extended to these "reactive" solutions, both in terms of total correlations and direct correlations. In the latter case, a set of first order partial differential equations describing the system properties in terms of these direct correlation functions and reaction extents have been developed, though not solved explicitly. These equations rigorously and completely describe the solution provided the boundary conditions (reference values of the activities) and equilibrium constants of the reactions are known.

With the theoretical basis and thermodynamic consistency firmly established, these have been applied to a system of current engineering interest--that of solutions of strong electrolytes. The singularities caused by the coulombic potential have been shown to be

rigorously removed by the projection procedure. Then, a composite model based on the primitive-ion idea has been developed, but only roughly tested. It is based on the hard-sphere equation of state with the limiting laws of Debye and Hueckel. The form originates with the mean spherical approximation for mixtures of ions. Preliminary calculations show errors of less than five per cent in compressibilities, seven per cent in partial molar volumes, and eighteen per cent in activity coefficient derivatives. Improvements are expected with more careful modeling studies.

Besides these calculations, the model predicts some other interesting results. First, the Harned coefficient (to the lowest order in molality) is shown to be a weak function in ionic strength, except under some restricted conditions. Secondly, the electrostatic contributions from Debye-Hueckel and the mean spherical approximation, were shown to be expandable in a power series in Debye lengths, with the parametric form of the first several terms known. The dependence on ion charge size and density is known exactly; only the coefficients are model-dependent. Thus, coefficients determined from data on one salt can be used for all salts. These can be compared to the theoretical values obtained here for the mean spherical model. Thirdly, this formulation takes advantage of the strength of the fluctuation solution theory. The derivatives are modeled and properties are obtained from an accessible reference state and the change due to composition and density changes. In the case of salts, the overall concentration is low and only a few terms in the concentration expansion need

to be retained. It is expected that the extension of this formulation to salting effects in multicomponent solvents will also be successful.

Lastly, an experiment has been built and a procedure established by which the density dependence of salt solutions can be determined. The experiment is operational and procedure specified. The method for obtaining activities of salts at high pressure from these and available data has been outlined. This information allows the empirical constants to be evaluated from the experimental data.

In all, theoretical basis for consistent correlations of "reactive" solutions, in general, and for those based on direct correlation functions in particular has been established. A mathematical model which shows promise has been formulated, and an experimental apparatus constructed to finalize this model. But, although the purpose set forth for this work has been finished, the work itself is more of a starting point for the engineering applications. There are several directions to be taken in continuing this process. First, of course, is the determination of the model parameters, and testing, or even revising, it with known results. When complete, an explicit model for compressibilities, partial molar volumes and activities will be attained.

From here, this model can be applied to various systems, an important example being phase equilibrium of salt-containing solutions. Also, this model is applicable to systems of partially dissociating salts, but in this case the differential equations of Chapter 3 describe the system rather than the more simple results of Chapter 4. A solution procedure for these equations must be developed.

A totally different direction can be taken in applying the totally-dissociating component equations to systems other than strong electrolytes. This is presently being done for the "solution of groups" model of systems. Of course, many other "reactive" systems could be described using the general equations of Chapter 3, provided a model for the direct correlation function integrals is established, and a general solution procedure devised. Hopefully, the general results given here will indeed prove useful in predicting properties of "reactive" systems that cannot be modelled either as hard spheres or primitive ions.

APPENDIX A
DERIVATIONS OF PRINCIPAL RELATIONS

Material Balance--Equation (2-1)

The component vector, \underline{N}_0 , and species vector, \underline{N} , are connected by the properties of a set of reactions. To derive the expressions, the first group contains all the reactions involving only the components found in \underline{N}_0 as reactants. This labeled the first set of reactions, with r_1 reactions. For this set, $\underline{N}^{(1)}$ is defined as the vector of mole numbers of all n_1 products and reactants and $\underline{v}^{(1)}$ as the matrix of stoichiometric coefficients. A reference component is chosen for each reaction in the set and an intensive extent of reaction matrix $\underline{\xi}^{(1)}$ is defined by:

$$(\underline{\xi}^{(1)})_{k\alpha} = \begin{cases} \xi_k^{(1)} = \text{extent of reaction if } \alpha \text{ is the reference component for reaction } k. \text{ This quantity indicates the degree to which the reaction has proceeded. At equilibrium, its value is found from the equilibrium constant of the reaction.} \\ 0 & \text{if } \alpha \text{ is not the reference component for reaction } k. \end{cases}$$

with $k = 1, \dots, r_1$; and $\alpha = 1, \dots, n_o$. We also define a matrix $\underline{L}^{(1)}$ by:

$$(\underline{L}^{(1)})_{i\alpha} = \delta_{i\alpha} = \begin{cases} 1 & i=\alpha & i=1, \dots, n_1 \\ 0 & i \neq \alpha & \alpha=1, \dots, n_o \end{cases}$$

The material balance for the first set of reactions is then

$$\underline{N}^{(1)} = (\underline{L}^{(1)} + \underline{v}^{(1)} \underline{\xi}^{(1)}) \underline{N}_o \quad (\text{A-1})$$

Note that unlike that of others, the present $\underline{\xi}^{(1)}$ is an intensive quantity and its form depends on the choice of reference component for each reaction. This is necessary in order to complete the desired manipulations but does not cause any difficulty in practice.

Similarly, we have for the second set of reactions, which includes all species obtained by reactions among the original components and the species created in reaction set 1,

$$\begin{aligned} \underline{N}^{(2)} &= (\underline{L}^{(2)} + \underline{v}^{(2)} \underline{\xi}^{(2)}) \underline{N}^{(1)} = (\underline{L}^{(2)} + \underline{v}^{(2)} \underline{\xi}^{(2)}) (\underline{L}^{(1)} \\ &\quad + \underline{v}^{(1)} \underline{\xi}^{(1)}) \underline{N}_o \end{aligned} \quad (\text{A-2})$$

where the matrices superscripted (2) are analogous to those for the first set except they are of dimension $n_2 \times n_1$. The reference component in set 2 can be any reactant for that set, including a product of set 1.

Continuing the process through the first m sets which constitute r reactions to get to the equilibrium composition \underline{N} ,

$$\begin{aligned} \underline{N} = & (\underline{L}^{(m)} + \underline{v}^{(m)} \underline{\xi}^{(m)}) (\underline{L}^{(m-1)} + \underline{v}^{(m-1)} \underline{\xi}^{(m-1)}) \dots (\underline{L}^{(1)} \\ & + \underline{v}^{(1)} \underline{\xi}^{(1)}) \underline{N}_O \equiv \underline{W} \underline{N}_O \end{aligned} \quad (\text{A-3})$$

Partial Molar Properties-Equations (2-5) and (2-8)

Starting from the equations of equilibrium, (2-2) and (2-4)

we write

$$dG = 0 = d\underline{N}^T \underline{\mu} + \underline{N}^T d\underline{\mu} = d\underline{N}_O^T \underline{\mu}_O + \underline{N}_O^T d\underline{\mu}_O \quad (\text{A-4})$$

where $\underline{N}^T d\underline{\mu}$ and $\underline{N}_O^T d\underline{\mu}_O$ are zero by the Gibbs-Duhem equation. Continuing, we write from equation (2-1)

$$0 = d(\underline{W} \underline{N}_O)^T \underline{\mu} = d\underline{N}_O^T \underline{W}^T \underline{\mu} + \underline{N}_O^T d\underline{W}^T \underline{\mu} \quad (\text{A-5})$$

Now

$$\begin{aligned} d\underline{W}^T = & (\underline{L}^{(1)} + \underline{v}^{(1)} \underline{\xi}^{(1)})^T \dots (\underline{L}^{(m-1)} + \underline{v}^{(m-1)} \underline{\xi}^{(m-1)})^T (d\underline{\xi}^{(m)})^T (\underline{v}^{(m)})^T + \dots \\ & + (\underline{L}^{(1)} + \underline{v}^{(1)} \underline{\xi}^{(1)})^T \dots (d\underline{\xi}^{(\ell)})^T (\underline{v}^{(\ell)})^T \dots (\underline{L}^{(m)} + \underline{v}^{(m)} \underline{\xi}^{(m)})^T + \dots \\ & + (d\underline{\xi}^{(1)})^T (\underline{v}^{(1)})^T (\underline{L}^{(2)} + \underline{v}^{(2)} \underline{\xi}^{(2)})^T \dots (\underline{L}^{(m)} + \underline{v}^{(m)} \underline{\xi}^{(m)})^T \end{aligned}$$

So

$$d\bar{W}^T_{\underline{\mu}} = 0 \quad (A-6)$$

The above equations give

$$d\bar{N}^T_{\underline{O}}(\bar{W}^T_{\underline{\mu}}) = d\bar{N}^T_{\underline{O}\underline{\mu}}$$

Since the $(d\bar{N}_{\underline{O}})_{\alpha}$'s are independent at any \underline{N}, T, P , we have equation (2-5). Equation (2-6) is obtained by noting that in the same manner in which $d\bar{W}^T_{\underline{\mu}}$ is shown to be zero, it can be shown that

$$(\bar{W}^T_{\underline{\mu}})_{\alpha} = (\bar{L}^T_{\underline{\mu}}) = (\bar{\mu}_{\underline{O}})_{\alpha} \quad (A-7)$$

As pointed out in the main body, the η_0 -space derivative is a complex expression

$$\begin{aligned} \left. \frac{\partial}{\partial N_{\alpha}} \right|_{T, P, N_{\beta \neq \alpha}} &= \sum_i \left. \frac{\partial N_i}{\partial N_{\alpha}} \right|_{T, P, N_{\beta \neq \alpha}} \left. \frac{\partial}{\partial N_i} \right|_{T, P, N_{j \neq i}} \\ &= \sum_i \left. \frac{\partial \sum_{\beta} W_{i\beta} N_{\alpha\beta}}{\partial N_{\alpha}} \right|_{T, P, N_{\gamma \neq \alpha}} \left. \frac{\partial}{\partial N_i} \right|_{T, P, N_{j \neq i}} = \sum_i W_{i\alpha} \left. \frac{\partial}{\partial N_i} \right|_{T, P, N_{j \neq i}} \\ &\quad + \sum_{i\beta} N_{\alpha\beta} \left. \frac{\partial W_{i\beta}}{\partial N_{\alpha}} \right|_{T, P, N_{\gamma \neq \alpha}} \left. \frac{\partial}{\partial N_i} \right|_{T, P, N_{j \neq i}} \end{aligned}$$

but the simple expression is obtained

$$\overline{M}_{o\alpha} = \overline{M}_{\alpha} \quad \alpha = 1, \dots, n_o \quad (2-8)$$

Mixing Properties-Equations (2-12) and (2-18a)

The partial molar Gibbs energies of mixing can be evaluated as

$$\overline{\Delta G}^{\text{MIX}} = \underline{\mu} - \underline{\mu}^o = RT \underline{\ln \hat{a}} \quad (A-8)$$

and

$$\overline{\Delta G}_o^{\text{MIX}} = \underline{\mu}_o - \underline{\mu}_o^o = RT \underline{\ln \hat{a}}_o \quad (A-9)$$

so, we have

$$\underline{W} \overline{\Delta G}^{\text{MIX}} = \underline{W} \underline{\mu}^T - \underline{W} \underline{\mu}^o = \underline{\mu}_o - \underline{W} \underline{\mu}^o + \underline{\mu}_o^o - \underline{\mu}_o^o \quad (A-10)$$

which is equation (2-12). The general form of this equation in terms of extents of reaction and equilibrium constants is for the case of equation (2-14)

$$\begin{aligned} \underline{W} \overline{\Delta G}^{\text{MIX}} &= \overline{\Delta G}_o^{\text{MIX}} + R T \{ (\underline{\xi}^{(1)})^T \underline{\ln K}^{(1)} + (\underline{L}^{(1)} + \underline{v}^{(1)})^T \underline{\xi}^{(2)} \} \underline{\ln K}^{(2)} + \dots \\ &\quad + (\underline{L}^{(1)} + \underline{v}^{(1)})^T \underline{\xi}^{(2)} \} (\underline{L}^{(2)} + \underline{v}^{(2)})^T \underline{\xi}^{(3)} \dots \\ &\quad \times (\underline{L}^{(m-1)} + \underline{v}^{(m-1)})^T \underline{\xi}^{(m)} \} \underline{\ln K}^{(m)} \} \quad (A-11) \end{aligned}$$

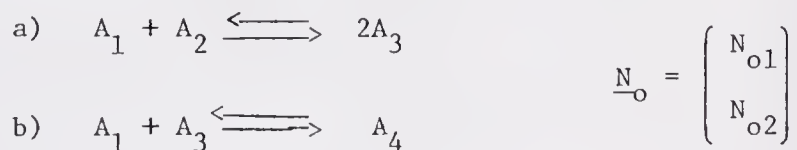
where $\underline{\ln K}^{(\ell)}$ is the vector of natural logarithms of the equilibrium constants for the reactions in set ℓ . Although appearing complicated, this is a straightforward relation to use.

APPENDIX B EXAMPLES OF THE PROJECTION PROCEDURE

A General Example

We first illustrate the general procedures given above by use of an example which should indicate the types of manipulations commonly encountered. Then we describe how the procedure would have been implemented in a case from the literature.

As an example of the construction of \underline{W} , a system can be constructed by mixing components A_1 and A_2 , which undergo the following reactions:



Reaction a) makes up set 1, and reaction b) makes up set 2.

The matrices for set 1 are:

$$\underline{v}^{(1)} = \begin{pmatrix} -1 \\ -1 \\ 2 \end{pmatrix}$$

$$\underline{\xi}^{(1)} = (\xi_a \quad 0) \quad \xi_a = \text{number of moles of 1 reacted by reaction a) divided by } N_{o1}$$

$$\underline{L}^{(1)} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \\ 0 & 0 \end{pmatrix}$$

By equation (A-1)

$$\begin{aligned} \underline{N}^{(1)} = \begin{pmatrix} N_1^{(1)} \\ N_2^{(1)} \\ N_3^{(1)} \end{pmatrix} &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \\ 0 & 0 \end{pmatrix} + \begin{pmatrix} -\xi_a & 0 \\ -\xi_a & 0 \\ 2\xi_a & 0 \end{pmatrix} \begin{pmatrix} N_{o1} \\ N_{o2} \end{pmatrix} \\ &= \begin{pmatrix} 1-\xi_a & 0 \\ -\xi_a & 1 \\ 2\xi_a & 0 \end{pmatrix} \begin{pmatrix} N_{o1} \\ N_{o2} \end{pmatrix} \end{aligned} \quad (\text{B-1})$$

For the second set

$$\underline{v}^{(2)} = \begin{pmatrix} -1 \\ 0 \\ -1 \\ 1 \end{pmatrix}$$

$$\underline{\xi}^{(2)} = (\xi_b \quad 0 \quad 0) \quad \xi_b = \text{number of moles of 1 reacted by reaction b), divided } N_1^{(1)}$$

$$\underline{L}^{(2)} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix}$$

$$\underline{N}^{(2)} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix} + \begin{pmatrix} -\xi_b & 0 & 0 \\ 0 & 0 & 0 \\ -\xi_b & 0 & 0 \\ \xi_b & 0 & 0 \end{pmatrix} \begin{pmatrix} N_1^{(1)} \\ N_2^{(1)} \\ N_3^{(1)} \end{pmatrix} = \begin{pmatrix} 1-\xi_b & 0 & 0 \\ 0 & 1 & 0 \\ -\xi_b & 0 & 1 \\ \xi_b & 0 & 0 \end{pmatrix} \begin{pmatrix} N_1^{(1)} \\ N_2^{(1)} \\ N_3^{(1)} \end{pmatrix}$$

Combining with equation (B-1) the composition of the system is given in terms of ξ_a , ξ_b , \underline{N}_o

$$\begin{aligned} \underline{N}^{(2)} = \underline{N} &= \begin{pmatrix} N_1 \\ N_2 \\ N_3 \\ N_4 \end{pmatrix} = \begin{pmatrix} 1-\xi_b & 0 & 0 \\ 0 & 1 & 0 \\ -\xi_b & 0 & 1 \\ \xi_b & 0 & 0 \end{pmatrix} \begin{pmatrix} 1-\xi_a & 0 \\ -\xi_a & 1 \\ 2\xi_a & 0 \end{pmatrix} \begin{pmatrix} N_{o1} \\ N_{o2} \end{pmatrix} \\ &= \begin{pmatrix} (1-\xi_a)(1-\xi_b)N_{o1} \\ N_{o2} - \xi_a N_{o1} \\ (2\xi_a - \xi_b + \xi_a \xi_b)N_{o1} \\ \xi_b(1-\xi_a)N_{o1} \end{pmatrix} \end{aligned} \quad (B-2)$$

For this system equation (B-2) gives \underline{W} as

$$\underline{W} = \begin{pmatrix} (1-\xi_a)(1-\xi_b) & 0 \\ -\xi_a & 1 \\ -\xi_b(1-\xi_a) + 2\xi_a & 0 \\ \xi_b(1-\xi_a) & 0 \end{pmatrix} \quad (B-3)$$

Of course, \underline{W} would be different if other reference components were used.

For the partial molar properties equation (2-8) yields

$$\bar{M}_1 = \left. \frac{\partial M}{\partial N_1} \right|_{T,P,N_2,N_3,N_4} = \left. \frac{\partial M}{\partial N_{o1}} \right|_{T,P,N_{o2}} = \bar{M}_{o1} \quad (\text{B-4a})$$

$$\bar{M}_2 = \bar{M}_{o2} \quad (\text{B-4b})$$

From equation (2-9) with reaction (a)

$$\bar{M}_3 = \frac{1}{2} (\bar{M}_1 + \bar{M}_2) = \frac{1}{2} (\bar{M}_{o1} + \bar{M}_{o2}) \quad (\text{B-4c})$$

From equation (2-9) with reaction (b)

$$\bar{M}_4 = \bar{M}_1 + \bar{M}_3 = \frac{3}{2} \bar{M}_{o1} + \frac{1}{2} \bar{M}_{o2} \quad (\text{B-4d})$$

For mixing properties equation (A-11) with equation (2-15) gives

$$\begin{pmatrix} (1-\xi_a)(1-\xi_b) & -\xi_a & -\xi_b(1-\xi_a) + 2\xi_a & \xi_b(1-\xi_a) \\ 0 & 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} \bar{\Delta M}_1^{\text{MIX}} \\ \bar{\Delta M}_2^{\text{MIX}} \\ \bar{\Delta M}_3^{\text{MIX}} \\ \bar{\Delta M}_4^{\text{MIX}} \end{pmatrix} =$$

$$\begin{pmatrix} \bar{\Delta M}_{o1}^{\text{MIX}} \\ \bar{\Delta M}_{o2}^{\text{MIX}} \end{pmatrix} + R \begin{pmatrix} \xi_a \\ 0 \end{pmatrix} f(T \ln K_a) + R \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$$

$$+ \left\{ \begin{pmatrix} \xi_a \\ 0 \end{pmatrix} \begin{pmatrix} -1 & -1 & -2 \end{pmatrix} \right\} \begin{pmatrix} \xi_b \\ 0 \end{pmatrix} f(T \ln K_b) \quad (\text{B-5a})$$

leading to the simple result $\overline{\Delta M}_2^{\text{MIX}} = \overline{\Delta M}_{o2}^{\text{MIX}}$ and

$$\begin{aligned} \overline{\Delta M}_1^{\text{MIX}}(1-\xi_a)(1-\xi_b) - \xi_a \overline{\Delta M}_2^{\text{MIX}} - \{\xi_b(1-\xi_a) - 2\xi_a\} \overline{\Delta M}_3^{\text{MIX}} + \overline{\Delta M}_4^{\text{MIX}} \xi_b(1-\xi_a) \\ = \overline{\Delta M}_{o1}^{\text{MIX}} + R\xi_a f(T \ln K_a) + R\xi_b(1-\xi_a) f(T \ln K_b) \end{aligned}$$

which can be reduced to

$$\overline{\Delta M}_1^{\text{MIX}} = \overline{\Delta M}_{o1}^{\text{MIX}} \quad (\text{B-5b})$$

only if $\mu_{o1}^o = \mu_1^o$. The simple form of these relations occurs because of cancellations. However, expressions for $\overline{\Delta M}_3^{\text{MIX}}$ and $\overline{\Delta M}_4^{\text{MIX}}$ are complex and generally not of interest.

Finally, for excess properties and activity coefficients, equation (2-20a) becomes

$$\begin{pmatrix} (1-\xi_a)(1-\xi_b) & -\xi_a & -\xi_b(1-\xi_a) + 2\xi_a & \xi_b(1-\xi_a) \\ 0 & 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} \overline{G}_1^E \\ \overline{G}_2^E \\ \overline{G}_3^E \\ \overline{G}_4^E \end{pmatrix} = \begin{pmatrix} \overline{G}_{o1}^E \\ \overline{G}_{o2}^E \end{pmatrix}$$

$$\begin{aligned}
& + R T \begin{pmatrix} \xi_a \\ 0 \end{pmatrix} \ln K_a + RT \left\{ \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} + \begin{pmatrix} \xi_a \\ 0 \end{pmatrix} \begin{pmatrix} -1 & -1 & 2 \end{pmatrix} \right\} \begin{pmatrix} \xi_a \\ 0 \\ 0 \end{pmatrix} \ln K_b \\
& + R T \begin{pmatrix} \ln x_{o1} \\ \ln x_{o2} \end{pmatrix} - \begin{pmatrix} (1-\xi_a)(1-\xi_b) & -\xi_a & -\xi_b(1-\xi_a) + 2\xi_a & \xi_b(1-\xi_a) \\ 0 & 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ln x_1 \\ \ln x_2 \\ \ln x_3 \\ \ln x_4 \end{pmatrix}
\end{aligned}$$

After considerable algebra, this reduces to what would be expected

$$\bar{G}_\alpha^E = \bar{G}_{o\alpha}^E + R_g T \{ \ln x_{o\alpha} - \ln x_\alpha \} \quad \alpha = 1, 2 \quad (\text{B-6})$$

For the reference states given above

$$\ln \gamma_{o\alpha} = \ln \gamma_\alpha + \ln(x_\alpha/x_{o\alpha}) \quad \alpha = 1, 2$$

$$\begin{aligned}
\text{with } x_1 &\equiv \frac{N_1}{N} = \frac{\sum_{\alpha} w_{1\alpha} N_{o\alpha}}{\sum_{i\alpha} w_{i\alpha} N_{o\alpha}} & x_{o1} &\equiv N_{o1} / \sum_{\alpha} N_{o\alpha} \\
&= 1 - x_2 & &= 1 - x_{o2}
\end{aligned}$$

Then, for this example

$$\ln \gamma_{o1} = \ln \gamma_1 - \ln \left(\frac{1-\xi_b(1-\xi_a)x_{o1}}{(1-\xi_a)(1-\xi_b)} \right) \quad (\text{B-7})$$

If the extents of reaction are arbitrarily set, equation (B-7) can be used directly in equation (2-21a) along with a model for $\ln\gamma_1$. If "equilibrium" is assumed, then ξ_a , ξ_b , x_1 , x_2 , x_3 and x_4 must be found from equations (2-1) and (A-11) specified values of x_{o1} , K_a and K_b , and a model for the γ_i . In this case, the expressions are

$$x_1 = \frac{(1-\xi_a)(1-\xi_b)x_{o1}}{1-\xi_b(1-\xi_a)x_{o1}} \quad (\text{B-8a})$$

$$x_2 = \frac{1-(1+\xi_a)x_{o1}}{1-(1-\xi_a)\xi_b x_{o1}} \quad (\text{B-8b})$$

$$x_3 = \frac{\{2\xi_a - \xi_b(1-\xi_a)\}x_{o1}}{1-(1-\xi_a)\xi_b x_{o1}} \quad (\text{B-8c})$$

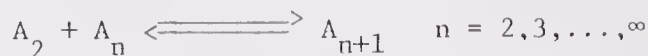
$$x_4 = 1 - x_1 - x_2 - x_3 \quad (\text{B-8d})$$

$$K_a = (\gamma_3 x_3)^2 / (\gamma_1 x_1 \gamma_2 x_2) \quad (\text{B-8e})$$

$$K_b = \gamma_4 x_4 / (\gamma_1 x_1 \gamma_3 x_3) \quad (\text{B-8f})$$

An Example of Continuous Association in the Chemical Theory

Prausnitz (1969: Sections 7.13 and 7.14) gives two examples of the chemical theory. In the first, all degrees of association are allowed among an alcohol (2) in a hydrocarbon (1). Thus, starting with N_{o1} moles of hydrocarbon and N_{o2} moles of alcohol, there are continued successive reactions



If, for each reaction (ℓ), we choose the reference component to be the n -mer, then the mole vectors have elements $(\underline{N}^{(\ell)})_n$ for $n \geq 2$, $\ell \geq 1$. The stoichiometric vectors have elements

$$(\underline{v}^{(1)})_2 = -2 ; (\underline{v}^{(1)})_3 = 1$$

$$(\underline{v}^{(\ell)})_2 = -1 = (\underline{v}^{(\ell)})_{\ell+1} ; (\underline{v}^{(\ell)})_{\ell+2} = 1 ;$$

$$(\underline{v}^{(\ell)})_i = 0 , i \neq 2, \ell+1, \ell+2; \ell \geq 2$$

The extent of reaction vectors have elements

$$(\underline{\xi}^{(n-1)})_n \equiv \xi_{n-1} = \frac{N_{n+1}^{(n-1)}}{N_n^{(n-2)}} ; (\underline{\xi}^{(\ell)})_k = 0, k \neq \ell+1; n \geq 1 \quad (\text{B-9})$$

and two important stoichiometric relationships are

$$N_2^{(\ell)} = \left\{ 1 - \xi_1 \left(2 + \sum_{k=2}^{\ell} \frac{k}{k-1} k' \right) \right\} N_{O2} \quad \ell \geq 2 \quad (\text{B-10a})$$

$$N_{n+1}^{(\ell)} = \left(\prod_{k=1}^{\ell} \xi_k \right) N_{O2} \quad \ell \geq 1 \quad (\text{B-10b})$$

The projector matrix is then

$$\underline{W}^T = \begin{pmatrix} 1 & 0 & 0 & \dots & 0 & \dots \\ 0 & \frac{N_2}{N_{O2}} & (1 - \xi_2)\xi_1 & \dots & (1 - \xi_{\ell-1}) \prod_{k=1}^{\ell-2} \xi_k & \dots \end{pmatrix} \quad (\text{B-11})$$

where N_i is the value $\lim_{\ell \rightarrow \infty} (N^{(\ell)})_i = \{1 - \xi_1 (2 + \sum_{k=2}^{\infty} \prod_{k'=2}^k \xi_{k'})\} N_{O2}$.

While these could be used in equation (2-16a), here their use is much simpler in equation (2-16b) and thus in equation (2-22).

The expression chosen for the Gibbs free energy of mixing of the species is obtained from two contributions (Renon and Prausnitz, 1967).

$$\underline{\Delta G}^{\text{MIX}} = \underline{\Delta G}_c^{\text{MIX}} + \underline{\Delta G}_p^{\text{MIX}}$$

The first (chemical) is for forming a lattice of hydrogen-bonded alcohol species at the volume fraction of the solution from a reference state of the pure, crystalline, oriented species. The second term (physical) is a simple Van Laar expression for interactions on the lattice in the solution of species. These yield for the species (including hydrocarbon)

$$\begin{aligned} (\underline{\Delta G}^{\text{MIX}})_1 / RT &= \{(\underline{\Delta G}_c^{\text{MIX}})_1 + (\underline{\Delta G}_p^{\text{MIX}})_1\} / RT \\ &= \{\ln \Phi_1 + (1 - \Phi_1) - v_1 \sum_{i=2}^{\infty} N_i / \sum_{j=1}^{\infty} v_j N_j\} \\ &+ v_1 \{(\sum_{i=2}^{\infty} \beta_{1i} \Phi_i)(\sum_{i=2}^{\infty} \Phi_i) \\ &- \sum_{i=2}^{\infty} \sum_{j=2}^{\infty} \beta_{ij} \Phi_i \Phi_j\} / RT \end{aligned} \quad (\text{B-12a})$$

$$\begin{aligned}
(\underline{\Delta G}^{\text{MIX}})_i / RT &= \{(\underline{\Delta G}^{\text{MIX}})_c\}_i + (\underline{\Delta G}^{\text{MIX}})_p\}_i / RT \\
&= \ln(\phi_i / v_i) - \frac{v_i}{v_1} \{\phi_1 + \ln(\tau+1) - 1\} - \frac{v_i \sum_{j=2}^{\infty} N_j}{\sum_{j=1}^{\infty} v_j N_j} \\
&\quad + \ln(\tau+1) + \ln(2v_1) \\
&\quad + v_i \left\{ \phi_1 (\beta_{1i} - \sum_{j=2}^{\infty} \beta_{1j} \phi_j) + \sum_{j=2}^{\infty} \phi_j (2\beta_{ij} \right. \\
&\quad \left. - \sum_{j'=2}^{\infty} \beta_{jj'} \phi_{j'}) \right\} \tag{B-12b}
\end{aligned}$$

Using equation (2-22), the desired activity coefficients are

$$\begin{aligned}
\ln \gamma_{o1} &= \ln(\phi_1 / x_{o1}) + (1 - \phi_1) - \frac{v_{o1}}{v_{o2}} \sum_{i=2}^{\infty} \phi_i / (v_i / v_{o2}) \\
&\quad + \frac{v_{o1}}{RT} \left\{ (1 - \phi_1) \sum_{i=2}^{\infty} \beta_{1i} \phi_i - \sum_{i=2}^{\infty} \sum_{j=2}^{\infty} \beta_{ij} \phi_i \phi_j \right\} \tag{B-13a}
\end{aligned}$$

$$\begin{aligned}
\ln \gamma_{o2} &= \ln(\phi_2 / \phi_2^o x_{o2}) - \frac{v_{o2}}{v_{o1}} \phi_1 - \sum_{j=2}^{\infty} (\phi_j - \phi_j^o) / (v_j / v_{o2}) \\
&\quad + \frac{v_{o2}}{RT} \left\{ \phi_1 (\beta_{12} - \sum_{j=2}^{\infty} \beta_{1j} \phi_j) \right.
\end{aligned}$$

$$+ \sum_{j=2}^{\infty} [2\beta_{2j}(\phi_j - \phi_j^0) - \sum_{j'=2}^{\infty} (\phi_j \phi_{j'} - \phi_j^0 \phi_{j'}^0) \beta_{jj'}] \} \quad (\text{B-13b})$$

Other than the basic models, no assumptions have been made. Yet the results are readily found from (2-22).

Major simplifications appear if it is assumed that the volumes are additive

$$v_i/v_{o2} = i - 1 \quad (\text{B-14})$$

that the physical interactions are independent of polymerization

$$\beta_{1j} \equiv \beta_{12}, \quad j \geq 2; \quad \beta_{ij} \equiv \beta_{22}, \quad i, j \geq 2 \quad (\text{B-15})$$

and that the polymerization reactions are independent of polymerization and are expressed by

$$\xi_k = K\phi_2 \equiv \xi \quad ; \quad k \geq 2 \quad (\text{B-16})$$

where K is a function of temperature only. (Because of the difference of the dimerization reaction ξ_1 is different from ξ .) These assumptions used in equation (B-10b) yield

$$\phi_i = (i-1)(K\phi_2)^{i-1} \phi_2 \quad i \geq 3 \quad (\text{B-17a})$$

$$\phi_{o2} = \sum_{i=2}^{\infty} \phi_i = \phi_2 / (1 - K\phi_2)^2 \quad (\text{B-17b})$$

$$\sum_{i=2}^{\infty} \Phi_i / (i-1) = \Phi_2 / (1 - K\Phi_2) \quad (\text{B-17c})$$

A value for Φ_2 can be found in terms of K and Φ_{O2} from (B-17b). A value for ξ_1 can be found from equations (B-17b) and (B-10a); here it is $K\Phi_2(1-K\Phi_2)$. Using equations (B-17) in (B-13) yields the results of Renon and Prausnitz (1967). The difference in the derivations are that we do not need to define the relationship for the equilibrium constant K in terms of any model and that the procedure is independent of the particular lattice model chosen. Introducing alternative assumptions about the reactions (e.g., 1st K for the dimerization reaction be different from that for other reactions) would change only equations (B-17) and the precise expressions are easily found from equations (B-13).

APPENDIX C
EXPRESSIONS FOR THE UNIQUAC AND UNIFAC MODELS

In both the UNIQUAC and UNIFAC models, the excess Gibbs energy is the sum of two terms.

$$G_o^E = (G_o^E)_{\text{combinatorial}} + (G_o^E)_{\text{residual}} \quad (\text{C-1})$$

For both models, the combinatorial parts are the same. For UNIQUAC, the parameters r_α and q_α are for molecules while for UNIFAC, they are obtained by projection of the group parameters R_i and Q_i .

$$\begin{aligned} r_\alpha &= \sum_i v_{i\alpha} R_i \\ q_\alpha &= \sum_i v_{i\alpha} Q_i \end{aligned} \quad (\text{C-2})$$

$$\begin{aligned} (G^E/RT)_{\text{combinatorial}} &= - (S^E/R)_{\text{athermal}} = \sum_\alpha N_{\alpha\alpha} \ln(\phi_\alpha/x_{\alpha\alpha}) \\ &+ \frac{1}{2} z \sum_\alpha N_{\alpha\alpha} q_\alpha \ln(\theta_\alpha/\phi_\alpha) \end{aligned} \quad (\text{C-3a})$$

In UNIQUAC

$$(G_o^E/RT)_{\text{residual}} = - \sum_\alpha N_{\alpha\alpha} q_\alpha \ln \left[\sum_\beta \theta_\beta \exp(-\Delta u_{\beta\alpha}/RT) \right] \quad (\text{C-3b})$$

and ϕ_α and θ_α are volume and surface fractions for the component α .

In UNIFAC

$$\left(\frac{G_o^E}{RT} \right)_{\text{residual}} = - \sum_\alpha N_{\alpha\alpha} \left\{ \sum_k v_{k\alpha} Q_k \left[\ln \left\{ \sum_m \theta_m \exp(-\Delta U_{mk}/RT) \right\} \right] \right\}$$

$$- \ln \left\{ \sum_m \Theta_m^{(\alpha)} \exp(-\Delta U_{mk}/RT) \right\} \} \} \quad (C-4)$$

where Θ_m is the group surface fraction, $\Theta_m^{(\alpha)}$ is Θ_m in a solution of pure α .

In the UNIQUAC model for molecules, the total interaction energy, U , is given by

$$U = \frac{1}{2} z \sum_{\alpha} N_{o\alpha} q_{\alpha} \sum_{\beta} \theta_{\beta\alpha} u_{\beta\alpha} \quad (C-5)$$

where

$$\theta_{\beta\alpha} = \frac{N_{o\beta} q_{\beta} \exp(-\Delta u_{\beta\alpha}/RT)}{\sum_{\gamma} N_{o\gamma} q_{\gamma} \exp(-\Delta u_{\gamma\alpha}/RT)} \equiv \frac{N_{o\beta} q_{\beta}^{\tau} \beta_{\alpha}}{\sum_{\gamma} N_{o\gamma} q_{\gamma}^{\tau} \gamma_{\alpha}}$$

$$\Delta u_{\gamma\alpha} = \frac{z}{2} [u_{\gamma\alpha} - u_{\alpha\alpha}]$$

In the UNIFAC model for groups, U is

$$U = \frac{1}{2} z \sum_i N_i Q_i \sum_j \Theta_{ji} U_{ji} \quad (C-6)$$

with

$$\Theta_{ji} = \frac{N_j Q_j \exp(-\Delta U_{ji}/RT)}{\sum_k N_k Q_k \exp(-\Delta U_{ki}/RT)} \equiv \frac{N_j Q_j^{\Psi} \psi_{ji}}{\sum_k N_k Q_k^{\Psi} \psi_{ki}}$$

$$\Delta U_{ki} = \frac{z}{2} [U_{ki} - U_{ii}]$$

The partial molar energies for UNIQUAC are

$$\bar{U}_{o\eta} = \frac{1}{2} z \sum_{\beta} \frac{q_{\eta} N_{o\beta} q_{\beta} u_{\beta\eta} \exp(-\Delta u_{\beta\eta}/RT)}{\sum_{\gamma} N_{o\gamma} q_{\gamma} \exp(-\Delta u_{\gamma\eta}/RT)} + \frac{1}{2} z \sum_{\alpha} \frac{q_{\eta} N_{o\alpha} q_{\alpha} u_{\eta\alpha} \exp(-\Delta u_{\eta\alpha}/RT)}{\sum_{\gamma} N_{o\gamma} q_{\gamma} \exp(-\Delta u_{\gamma\alpha}/RT)}$$

$$- \frac{1}{2} z \sum_{\alpha} q_{\eta} N_{o\alpha} q_{\alpha} \sum_{\beta} \frac{N_{o\beta} q_{\beta} u_{\beta\alpha} \exp(-\Delta u_{\beta\alpha}/RT) \exp(-\Delta u_{\eta\alpha}/RT)}{\left(\sum_{\gamma} N_{o\gamma} q_{\gamma} \exp(-\Delta u_{\gamma\alpha}/RT) \right)^2} \quad (C-7)$$

and for UNIFAC

$$\begin{aligned} \bar{U}_{\ell} = & \frac{1}{2} z \sum_j \frac{Q_{\ell} N_j Q_j U_{j\ell} \exp(-\Delta U_{j\ell}/RT)}{\sum_k N_k Q_k \exp(-\Delta U_{k\ell}/RT)} + \frac{1}{2} z \sum_i \frac{Q_{\ell} N_i Q_i U_{\ell i} \exp(-\Delta U_{\ell i}/RT)}{\sum_k N_k Q_k \exp(-\Delta U_{ki}/RT)} \\ & + \frac{1}{2} z \sum_i Q_{\ell} N_i Q_i \sum_j \frac{N_j Q_j U_{ji} \exp(-\Delta U_{ji}/RT) \exp(-\Delta U_{\ell i}/RT)}{\left(\sum_k Q_k N_k \exp(-\Delta U_{ki}/RT) \right)^2} \end{aligned} \quad (C-8)$$

To test the projections of equation (2-32), we must first make the standard projections, $q_{\eta} = \sum_p v_{p\eta} Q_p$ and $N_{\ell} = \sum_{\epsilon} v_{\ell\epsilon} N_{o\epsilon}$ to write:

$$\begin{aligned} \sum_{\ell} v_{\ell\eta} \bar{U} = & \frac{1}{2} z \sum_{\lambda} \sum_{\alpha} \sum_j \frac{v_{\ell\eta} Q_{\ell} v_{j\alpha} N_{o\alpha} Q_j U_{j\ell} \exp(-\Delta U_{j\ell}/RT)}{\sum_{k\gamma} v_{k\gamma} N_{o\gamma} Q_k \exp(-\Delta U_{k\ell}/RT)} \\ & + \frac{1}{2} z \sum_{\lambda} \sum_{\alpha} \sum_j \frac{v_{\ell\eta} Q_{\ell} v_{j\alpha} N_{o\alpha} Q_j U_{\ell j} \exp(-\Delta U_{\ell j}/RT)}{\sum_{k\gamma} v_{k\gamma} N_{o\gamma} Q_k \exp(-\Delta U_{kj}/RT)} \\ & - \frac{1}{2} z \sum_{\lambda} \sum_{\alpha} \sum_j \sum_{\beta} \frac{v_{\ell\eta} Q_{\ell} v_{j\alpha} N_{o\alpha} Q_j v_{i\beta} N_{o\beta} Q_i U_{ji} \exp(-\Delta U_{ji}/RT) \exp(-\Delta U_{\ell i}/RT)}{\left(\sum_{k\gamma} v_{k\gamma} N_{o\gamma} Q_k \exp(-\Delta U_{ki}/RT) \right)^2} \end{aligned} \quad (C-9)$$

while

$$\begin{aligned} \bar{U}_{o\eta} = & \frac{1}{2} z \sum_{\lambda} \sum_{\alpha} \sum_j \frac{v_{\ell\eta} Q_{\ell} v_{j\alpha} N_{o\alpha} Q_j u_{\alpha\eta} \exp(-\Delta u_{\alpha\eta}/RT)}{\sum_{k\gamma} v_{k\gamma} N_{o\gamma} Q_k \exp(-\Delta u_{\gamma\eta}/RT)} \\ & + \frac{1}{2} z \sum_{\lambda} \sum_{\alpha} \sum_j \frac{v_{\ell\eta} Q_{\ell} v_{j\alpha} N_{o\alpha} Q_j u_{\eta\alpha} \exp(-\Delta u_{\eta\alpha}/RT)}{\sum_{k\gamma} v_{k\gamma} N_{o\gamma} Q_k \exp(-\Delta u_{\gamma\alpha}/RT)} \end{aligned} \quad (C-10)$$

$$- \frac{1}{2} z \sum_{\ell} \sum_{\alpha} \sum_{j} \sum_{\beta} \sum_{i} \frac{v_{\ell\eta}^{Q_{\ell}} v_{j\alpha}^{N_{o\alpha}} v_{i\beta}^{Q_j} v_{o\beta}^{N_{o\beta}} v_{i\beta}^{Q_i} u_{\beta\alpha} \exp(-\Delta u_{\beta\alpha}/RT) \exp(-\Delta u_{\eta\alpha}/RT)}{\left(\sum_{k\gamma} v_{k\gamma}^{N_{o\gamma}} Q_k \exp(-\Delta u_{\gamma\alpha}/RT) \right)^2}$$

It is apparent that the two equations cannot be made identical, because the ΔU_{ij} , etc., will not be the same as $\Delta u_{\alpha\eta}$, etc., in the summations. If the projections of q and N are made, the "Boltzmann-factor weighted" projection of the surface fractions cannot be made, without a loss of consistency.

APPENDIX D
CONSTRUCTION OF MATRICES FOR
GENERAL MATERIAL BALANCE

Here we consider the material balance and associated matrices in the general case of subsequent reactions. First

$$\underline{N} = \underline{W}\underline{N}_0$$

where

$$\begin{aligned} \underline{W} = & [\underline{L}^{(m)} + \underline{v}^{(m)} \underline{\xi}^{(m)}] [\underline{L}^{(m-1)} + \underline{v}^{(m-1)} \underline{\xi}^{(m-1)}] \dots [\underline{L}^{(\ell)} + \underline{v}^{(\ell)} \underline{\xi}^{(\ell)}] \dots \\ & [\underline{L}^{(2)} + \underline{v}^{(2)} \underline{\xi}^{(2)}] [\underline{L}^{(1)} + \underline{v}^{(1)} \underline{\xi}^{(1)}] \end{aligned} \quad (D-1)$$

as derived in Appendix A. When the matrices are divided into blocks as defined in equations (3-3) to (3-5), equation (D-1) can be rewritten

$$\underline{W} = \underline{W}^{(m)} \underline{W}^{(m-1)} \dots \underline{W}^{(\ell)} \dots \underline{W}^{(2)} \dots \underline{W}^{(1)}$$

where

$$\underline{W}^{(\ell)} = \begin{pmatrix} \underline{I} + \underline{v}_C^{(\ell)} \underline{\xi}^{(\ell)} \\ \underline{v}_D^{(\ell)} \underline{\xi}^{(\ell)} \\ \underline{v}_I^{(\ell)} \underline{\xi}^{(\ell)} \end{pmatrix} \quad n_\ell \times n_{\ell-1} \quad (D-2)$$

By analogy to equations (3-8) and (3-13) we define $\underline{Z}_0^{(\ell)}$ and $\underline{Y}^{(\ell)}$ by the equations

$$\underline{Z}_O^{(\ell)} = \begin{pmatrix} \underline{0} \\ -(\underline{v}_D^{(\ell)})^T -1 \quad \underline{v}_I^{(\ell)T} \\ \underline{I} \end{pmatrix} \quad n_\ell \times (n_\ell - n_{\ell-1} - r) \quad (D-3)$$

$$\underline{Y}^{(\ell)} = \begin{pmatrix} \underline{I} \\ -(\underline{v}_D^{(\ell)})^T -1 \quad \underline{v}_C^{(\ell)T} \\ \underline{0} \end{pmatrix} \quad n_\ell \times n_{\ell-1} \quad (D-4)$$

As before,

$$\underline{Z}_O^{(\ell)T} \underline{W}^{(\ell)} = \underline{0} \quad (D-5a)$$

and

$$\underline{Y}^{(\ell)T} \underline{W}^{(\ell)} = \underline{I} \quad (D-5b)$$

Now the overall \underline{Y} and \underline{Z}_O matrices can be constructed. The \underline{Y} matrix is the more straightforward, being

$$\underline{Y} = \underline{Y}^{(m)} \underline{Y}^{(m-1)} \dots \underline{Y}^{(\ell)} \dots \underline{Y}^{(2)} \underline{Y}^{(1)} \quad (n \times n_0) \quad (D-6)$$

From equation (D-5b) it can be easily seen that $\underline{Y}^T \underline{W} = \underline{I}$ as required.

The construction of the \underline{Z}_O matrix is less obvious. The first

$n \times (n - n_{m-1} - r_m)$ columns are $\underline{Z}_O^{(m)}$ since

$$\underline{Z}_O^{(m)} \underline{W} = \underline{Z}_O^{(m)T} \underline{W}^{(m)} \underline{W}^{(m-1)} \dots \underline{W}^{(\ell)} \dots \underline{W}^{(1)} = \underline{0}$$

The next $n \times (n_{m-1} - n_{m-2} - r_{m-1})$ columns of \underline{Z}_O are $\underline{Y}^{(m)} \underline{Z}_O^{(m-1)}$.

$$\begin{aligned} [\underline{Y}^{(m)} \underline{Z}_O^{(m-1)}]^T \underline{W} &= \underline{Z}_O^{(m-1)T} \underline{Y}^{(m)T} \underline{W}^{(m)} \underline{W}^{(m-1)} \underline{W}^{(m-2)} \dots \underline{W}^{(1)} \\ &= \underline{Z}_O^{(m-1)T} \underline{W}^{(m-1)} \underline{W}^{(m-2)} \dots \underline{W}^{(1)} = \underline{0} \end{aligned}$$

where equations (D-5) have been employed. Continuing in an analogous manner, the \underline{Z}_0 matrix can be constructed by juxtaposing m submatrices and has the form

$$\underline{Z}_0 = [\underline{Z}_0^{(m)}; \underline{Y}^{(m)} \underline{Z}_0^{(m-1)}; \dots; \underline{Y}^{(m)} \underline{Y}^{(m-1)} \dots \underline{Y}^{(\ell+1)} \underline{Z}_0^{(\ell)}; \dots; \underline{Y}^{(m)} \underline{Y}^{(m-1)} \dots \underline{Y}^{(3)} \underline{Z}_0^{(2)}; \underline{Y}^{(m)} \underline{Y}^{(m-1)} \dots \underline{Y}^{(2)} \underline{Y}^{(2)} \underline{Z}_0^{(1)}]$$

(D-7)

The total number of columns of \underline{Z}_0 is

$$\begin{aligned} & (n - n_{m-1} - r_m) + (n_{m-1} - n_{m-2} - r_{m-1}) + \dots + (n_\ell - n_{\ell-1} - r) + \dots \\ & + (n_2 - n_1 - r_2) + (n_1 - n_0 - r_1) = n - n_0 + \sum_{\ell=1}^m r_m = n - n_0 - r \end{aligned}$$

So, the dimensions of \underline{Z}_0 are $n \times (n - n_0 - r)$ as required.

The \underline{U} and \underline{Z}_1 matrices cannot be written explicitly in the general case and so are simply defined by equations (3-9) and (3-11). However, they are not explicitly used either.

APPENDIX E
DERIVATIVES WITH RESPECT TO THE COMPONENT
CHEMICAL POTENTIALS

The derivatives of the grand partition function (Ξ) and the average composition vectors ($\langle \underline{N} \rangle$ or \underline{N}_0) with respect to component chemical potentials ($\underline{\mu}_0$ or $\underline{\ln \lambda}$) are treated in detail below. The difficulty in evaluating these derivatives stems from the fact that the vector of Lagrange multipliers in the constraint space, $\underline{\ln \theta}$, is by necessity a function of those in component space, $\underline{\ln \lambda}$.

Allowing \underline{v} to represent the matrix of stoichiometric coefficients of all n species in all r reactions (regardless of reaction set), the equations of reaction equilibria are

$$\underline{v}^T \underline{\mu} = \underline{0} \quad (2-4)$$

or, partitioning the matrices as in equation (3-5)

$$(\underline{v}_C^T \quad \underline{v}_D^T \quad \underline{v}_I^T) \begin{pmatrix} \underline{\mu}_C \\ \underline{\mu}_D \\ \underline{\mu}_I \end{pmatrix} = \underline{v}_C^T \underline{\mu}_C + \underline{v}_D^T \underline{\mu}_D + \underline{v}_I^T \underline{\mu}_I = \underline{0} \quad (E-1)$$

Differentiating with respect to $\ln \lambda_\alpha$ ($= \beta \mu_{0\alpha}$) and noting that $\underline{\mu}_C = \underline{\mu}_D$ as per equation (2-6), equation (E-1) becomes

$$\underline{v}_C^T \underline{e}_\alpha + \underline{v}_D^T \beta \left. \frac{\partial \underline{\mu}_D}{\partial \ln \lambda_\alpha} \right|_{T,V,\lambda_{\gamma \neq \alpha}} + \underline{v}_I^T \beta \left. \frac{\partial \underline{\mu}_I}{\partial \ln \lambda_\alpha} \right|_{T,V,\lambda_{\gamma \neq \alpha}} = \underline{0} \quad (E-2)$$

Using the fact that \underline{v}_D is nonsingular by construction, we premultiply by $(\underline{v}_D^T)^{-1}$ and rearrange to

$$\beta \left. \frac{\partial \underline{\mu}_D}{\partial \ln \lambda} \right|_{T,V,\lambda_{\gamma \neq \alpha}} = -(\underline{v}_D^T)^{-1} \underline{v}_C^T \underline{e}_{-\alpha} - (\underline{v}_D^T)^{-1} \underline{v}_C^T \left. \beta \frac{\partial \underline{\mu}_I}{\partial \ln \lambda} \right|_{T,V,\lambda_{\gamma \neq \alpha}} \quad (E-3)$$

Next, equation (3-25) is differentiated with respect to $\beta^{-1} \ln \lambda_{\alpha}$, and again, the $\underline{\mu}$ vector is partitioned, giving

$$\beta \left. \frac{\partial \underline{\mu}}{\partial \ln \lambda} \right|_{T,V,\lambda_{\gamma \neq \alpha}} = \begin{pmatrix} \underline{e}_{-\alpha} \\ \beta \left. \frac{\partial \underline{\mu}_D}{\partial \ln \lambda} \right|_{T,V,\lambda_{\gamma \neq \alpha}} \\ \beta \left. \frac{\partial \underline{\mu}_I}{\partial \ln \lambda} \right|_{T,V,\lambda_{\gamma \neq \alpha}} \end{pmatrix} \quad (E-4a)$$

$$= \left. \frac{\partial \underline{U}}{\partial \ln \lambda} \right|_{T,V,\lambda_{\gamma \neq \alpha}} \frac{\ln \lambda}{\ln \lambda} + (\underline{U})_{\alpha} + \left. \frac{\partial \underline{Z}}{\partial \ln \lambda} \right|_{T,V,\lambda_{\gamma \neq \alpha}} \frac{\ln \lambda}{\ln \lambda} + \underline{Z} \left. \frac{\partial \ln \theta}{\partial \ln \lambda} \right|_{T,V,\lambda_{\gamma \neq \alpha}} \quad (E-4b)$$

Substituting equation (E-3) into (E-4a) gives, after rearrangement,

$$\begin{aligned} \beta \left. \frac{\partial \underline{\mu}}{\partial \ln \lambda} \right|_{T,V,\lambda_{\gamma \neq \alpha}} &= \begin{pmatrix} \underline{I} \\ -(\underline{v}_D^T)^{-1} \underline{v}_C^T \\ \underline{0} \end{pmatrix} \underline{e}_{-\alpha} + \begin{pmatrix} \underline{0} \\ -(\underline{v}_D^T)^{-1} \underline{v}_I^T \\ \underline{I} \end{pmatrix} \beta \left. \frac{\partial \underline{\mu}_I}{\partial \ln \lambda} \right|_{T,V,\lambda_{\gamma \neq \alpha}} \\ &= (\underline{Y})_{\alpha} + \underline{Z}_0 \beta \left. \frac{\partial \underline{\mu}_I}{\partial \ln \lambda} \right|_{T,V,\lambda_{\gamma \neq \alpha}} \end{aligned} \quad (E-5)$$

Finally, combination of equations (E-4b) and (E-5) leads to the dependence of $\underline{\ln\theta}$ on the $\ln\lambda_\alpha$'s, namely

$$\begin{aligned} \underline{Z} \frac{\partial \ln\theta}{\partial \ln\lambda_\alpha} \bigg|_{T,V,\lambda_{\gamma \neq \alpha}} &= (\underline{Y})_\alpha + \underline{Z}_0 \beta \frac{\partial \underline{\mu}_I}{\partial \ln\lambda_\alpha} \bigg|_{T,V,\lambda_{\gamma \neq \alpha}} - (\underline{U})_\alpha \\ &\quad - \frac{\partial \underline{Z}}{\partial \ln\lambda_\alpha} \bigg|_{T,V,\lambda_{\gamma \neq \alpha}} \frac{\ln\theta}{\ln\lambda_\alpha} - \frac{\partial \underline{U}}{\partial \ln\lambda_\alpha} \bigg|_{T,V,\lambda_{\gamma \neq \alpha}} \frac{\ln\lambda_\alpha}{\ln\lambda_\alpha} \end{aligned} \quad (E-6)$$

where the notation $(\underline{Y})_\alpha$ or $(\underline{U})_\alpha$ indicates the vector which comprises the α -th column of \underline{Y} or \underline{U} .

To examine the fluctuations, we look at the derivatives of the grand partition function. First, differentiation is carried out with respect to $\ln\lambda_\alpha$

$$\begin{aligned} \frac{1}{\Xi} \frac{\partial \Xi}{\partial \ln\lambda_\alpha} \bigg|_{T,V,\lambda_{\gamma \neq \alpha}} &= \frac{1}{\Xi} \sum_{\underline{N}} \sum_q \underline{N}^T \left[\frac{\partial \underline{U}}{\partial \ln\lambda_\alpha} \bigg|_{T,V,\lambda_{\gamma \neq \alpha}} \frac{\ln\lambda_\alpha}{\ln\lambda_\alpha} + (\underline{U})_\alpha + \frac{\partial \underline{Z}}{\partial \ln\lambda_\alpha} \bigg|_{T,V,\lambda_{\gamma \neq \alpha}} \frac{\ln\theta}{\ln\lambda_\alpha} \right. \\ &\quad \left. + \underline{Z} \frac{\partial \ln\theta}{\partial \ln\lambda_\alpha} \bigg|_{T,V,\lambda_{\gamma \neq \alpha}} \right] \exp[-\beta E_{\underline{N}q} + \underline{N}^T (\underline{U} \frac{\ln\lambda_\alpha}{\ln\lambda_\alpha} + \underline{Z} \frac{\ln\theta}{\ln\lambda_\alpha})] \end{aligned} \quad (E-7)$$

which, with equation (E-6), reduces to

$$\begin{aligned} \frac{1}{\Xi} \frac{\partial \Xi}{\partial \ln\lambda_\alpha} \bigg|_{T,V,\lambda_{\gamma \neq \alpha}} &= \langle \underline{N} \rangle^T \left[(\underline{Y})_\alpha + \underline{Z}_0 \beta \frac{\partial \underline{\mu}_I}{\partial \ln\lambda_\alpha} \bigg|_{T,V,\lambda_{\gamma \neq \alpha}} \right] \\ &= \langle \underline{N} \rangle^T (\underline{Y})_\alpha = N_{0\alpha} \end{aligned} \quad (E-8)$$

where equations (3-7) and (3-14a) were used to obtain the last two equalities. This result is what is expected since $\ln \lambda_\alpha = \beta \mu_{\alpha\alpha}$.

The quantities of greatest interest are the derivatives of average composition with respect to component chemical potentials.

$$\begin{aligned}
 \left. \frac{\partial \langle \underline{N} \rangle}{\partial \ln \lambda_\alpha} \right|_{T, V, \lambda_{\gamma \neq \alpha}} &= \left. \frac{\partial}{\partial \ln \lambda_\alpha} \right|_{T, V, \lambda_{\gamma \neq \alpha}} \left\{ \frac{1}{\Xi} \sum_{\underline{N}} \sum_{\underline{q}} \underline{N} \exp[-\beta E_{\underline{Nq}} + \underline{N}^T (\underline{U} \ln \lambda + \underline{Z} \ln \theta)] \right\} \\
 &= \langle \underline{N} \underline{N}^T \rangle \left\{ \left. \frac{\partial \underline{U}}{\partial \ln \lambda_\alpha} \right|_{T, V, \lambda_{\gamma \neq \alpha}} \ln \lambda + (\underline{U})_\alpha + \left. \frac{\partial \underline{Z}}{\partial \ln \lambda_\alpha} \right|_{T, V, \lambda_{\gamma \neq \alpha}} \ln \theta \right. \\
 &\quad \left. + \underline{Z} \left. \frac{\partial \ln \theta}{\partial \ln \lambda_\alpha} \right|_{T, V, \lambda_{\gamma \neq \alpha}} \right\} - \langle \underline{N} \rangle \frac{1}{\Xi} \left. \frac{\partial \Xi}{\partial \ln \lambda_\alpha} \right|_{T, V, \lambda_{\gamma \neq \alpha}} \quad (E-9)
 \end{aligned}$$

Equations (3-26), (D-6) and (D-8) allow this to be simplified to

$$\begin{aligned}
 \left. \frac{\partial \langle \underline{N} \rangle}{\partial \ln \lambda_\alpha} \right|_{T, V, \lambda_{\gamma \neq \alpha}} &= \left. \frac{\partial \langle \underline{N} \rangle}{\partial \mu_{\alpha\alpha}} \right|_{T, V, \mu_{\gamma \neq \alpha}} = \langle \underline{N} \underline{N}^T \rangle \left\{ (\underline{Y})_\alpha + \underline{Z}_\alpha \left. \frac{\partial \underline{\mu}_I}{\partial \mu_{\alpha\alpha}} \right|_{T, V, \mu_{\gamma \neq \alpha}} \right\} - \langle \underline{N} \rangle \underline{N}_{\alpha\alpha} \\
 &\quad (E-10)
 \end{aligned}$$

Finally, equation (E-10) can be projected into component space using equation (3-14a) and the fact that \underline{Y} is a constant matrix, giving

$$\underline{Y}^T \left. \frac{\partial \langle \underline{N} \rangle}{\partial \mu_{\alpha\alpha}} \right|_{T, V, \mu_{\gamma \neq \alpha}} = \left. \frac{\partial \underline{Y}^T \langle \underline{N} \rangle}{\partial \mu_{\alpha\alpha}} \right|_{T, V, \mu_{\gamma \neq \alpha}} = \left. \frac{\partial \underline{N}_{\alpha\alpha}}{\partial \mu_{\alpha\alpha}} \right|_{T, V, \mu_{\gamma \neq \alpha}}$$

which becomes equation (3-36), and, since $\langle \underline{N} \rangle^T \underline{Z}_0 = \underline{0}$, yields equation (3-37).

Another important relation that arises from $\langle \underline{N} \rangle^T \underline{Z}_0 = \underline{0}$ and the fact that \underline{Z}_0 is constant is

$$\underline{Z}_0^T \frac{\partial \langle \underline{N} \rangle}{\partial \beta_{\mu_{o\alpha}}} \bigg|_{T, V, \mu_{o_{\gamma \neq \alpha}}} = \underline{0} = \underline{Z}_0^T \frac{\langle \underline{N} \underline{N}^T \rangle}{\langle \underline{N} \rangle} \left((\underline{Y})_{\alpha} + \underline{Z}_0 \frac{\partial \underline{I}}{\partial \mu_{o\alpha}} \bigg|_{T, V, \mu_{o_{\gamma \neq \alpha}}} \right) \quad (\text{E-11})$$

This relation is used in Chapter 4.

APPENDIX F
PROJECTION OF INVERSE MOLE FRACTIONS OF LIMITING
REACTANTS IN THE LIMIT OF COMPLETE REACTIONS

Since \underline{X}_L^{-1} diverges in the limit of complete reactions, it is necessary to first project \underline{X}_L^{-1} by $(\underline{W}+\underline{K})$ at non-zero limiting reactant concentrations, then perform the limiting process. This is, of course, the rigorous way to evaluate the limit, but was unnecessary for the remainder of $(\underline{X}^{-1}-\underline{C})$.

In the general case (ξ 's unspecified),

$$\begin{aligned}
 (\underline{W}+\underline{K})_{i\beta} &= \delta_{i\beta} + \sum_{\alpha=n_s+1}^{n_o} v_{i\alpha} \xi_{\alpha}^{\delta} r_{\alpha} + \sum_{\gamma=1}^{n_o} N_{o\gamma} \sum_{\alpha=n_s+1}^{n_o} v_{i\alpha} \frac{\partial \xi_{\alpha}}{\partial N_{o\beta}} \bigg|_{T,V,N_{o\gamma \neq \beta}} \delta_{\gamma r_{\alpha}} \\
 &= \delta_{i\beta} + \sum_{\alpha=n_s+1}^{n_o} v_{i\alpha} \left[\xi_{\alpha}^{\delta} r_{\alpha} + N_{o\alpha} \frac{\partial \xi_{\alpha}}{\partial N_{o\beta}} \bigg|_{T,V,N_{o\gamma \neq \beta}} \right] \quad (F-1)
 \end{aligned}$$

and

$$\begin{aligned}
 \begin{pmatrix} 0 & 0 & 0 \\ 0 & \underline{X}_L^{-1} & 0 \\ 0 & 0 & 0 \end{pmatrix}_{ij} &= \begin{cases} \frac{1}{x_i} \delta_{ij} & \text{if } n_s+1 \leq i \leq n_o \\ 0 & \text{otherwise} \end{cases} \\
 &= \begin{cases} \frac{N \delta_{ij}}{N_{oi} + v_{ii} \xi_i N_{or_i}} & n_s+1 \leq i \leq n_o \\ 0 & \text{otherwise} \end{cases} \quad (F-2)
 \end{aligned}$$

The projection of the divergent matrix yields

$$\begin{aligned}
 & \left((\underline{W+K})^T \begin{pmatrix} \underline{0} & \underline{0} & \underline{0} \\ \underline{0} & \underline{X_L^{-1}} & \underline{0} \\ \underline{0} & \underline{0} & \underline{0} \end{pmatrix} (\underline{W+K}) \right)_{\beta\gamma} = N \sum_{i=n_s+1}^{n_o} \left(\delta_{i\beta} + \sum_{\alpha=n_s+1}^{n_o} v_{i\alpha} (\xi_\alpha \delta_{\beta\alpha} r_\alpha \right. \\
 & \left. + N_{or_\alpha} \frac{\partial \xi_\alpha}{\partial N_{o\beta}} \right)_{T,V,N_{o\gamma \neq \beta}} \times \left(\delta_{ir} + \sum_{\alpha=n_s+1}^{n_o} v_{i\alpha} (\xi_\alpha \delta_{\beta\alpha} r_\alpha \right. \\
 & \left. + N_{or_\alpha} \frac{\partial \xi_\alpha}{\partial N_{o\beta}} \right)_{T,V,N_{o\gamma \neq \beta}} \div (N_{oi} + v_{ii} \xi_i N_{or_i}) \quad (F-3)
 \end{aligned}$$

As ξ_α approaches its value for a complete reaction (equation 3-63)

$$\xi_\alpha = - \frac{1}{v_{\alpha\alpha}} \frac{N_{o\alpha}}{N_{or_\alpha}} - \epsilon_\alpha \quad (\epsilon_\alpha \leq 0) \quad (F-4)$$

where ϵ_α is positive and goes to zero as complete reaction is attained.

Also

$$\frac{\partial \xi_\alpha}{\partial N_{o\beta}} \bigg|_{T,V,N_{o\gamma \neq \beta}} = - \frac{1}{v_{\alpha\alpha}} \frac{N_{or_\alpha} \delta_{\alpha\beta} - N_{o\alpha} \delta_{\beta\alpha} r_\alpha}{N_{or_\alpha}^2} - \frac{\partial \xi_\alpha}{\partial N_{o\beta}} \bigg|_{T,V,N_{o\gamma \neq \beta}} \quad (F-5)$$

Since ξ_α is bounded ($0 \leq \xi_\alpha \leq - \frac{1}{v_{\alpha\alpha}} \frac{N_{o\alpha}}{N_{or_\alpha}}$) and the limit of $\frac{\partial \xi_\alpha}{\partial N_{o\beta}} \bigg|_{T,V,N_{o\gamma \neq \beta}}$

exists, the quantity $\frac{\partial \xi_\alpha}{\partial N_{o\beta}} \bigg|_{T,V,N_{o\gamma \neq \beta}}$ must also approach zero as

ϵ_α approaches zero. So, for small enough ϵ_α

$$\left. \frac{\partial \epsilon_\alpha}{\partial N_{o\beta}} \right|_{T,V,N_{o_{\gamma \neq \beta}}} = M_{\beta\alpha} \epsilon_\alpha / N_{or_\alpha} \quad (F-6)$$

where $M_{\beta\alpha}$ is always finite and of the same sign as $\left. \frac{\partial \epsilon_\alpha}{\partial N_{o\beta}} \right|_{T,V,N_{o_{\gamma \neq \alpha}}}$.

Substitution of the results of equations (F-4), (F-5) and (F-6) into equation (F-3) yields (for ξ_α 's very near their complete reaction values)

$$\begin{aligned} & \left(\begin{array}{c} (W+K)^T \begin{pmatrix} 0 & 0 & 0 \\ 0 & X_L^{-1} & 0 \\ 0 & 0 & 0 \end{pmatrix} (W+K) \end{array} \right)_{\beta\gamma} = N \sum_{i=n_s+1}^{n_o} \left(\left(\delta_{i\beta} + \sum_{\alpha=n_s+1}^{n_o} \left(-\frac{v_{i\alpha}}{v_{\alpha\alpha}} \delta_{\alpha\beta} - v_{i\alpha} \epsilon_\alpha \delta_{\beta r_\alpha} \right. \right. \right. \\ & \left. \left. \left. - v_{i\alpha} M_{\beta\alpha} \epsilon_\alpha \right) \times \left(\delta_{i\gamma} + \sum_{\alpha=n_s+1}^{n_o} \left(-\frac{v_{i\alpha}}{v_{\alpha\alpha}} \delta_{\alpha\gamma} - v_{i\alpha} \epsilon_\alpha \delta_{\alpha\gamma} - v_{i\alpha} M_{\gamma\alpha} \epsilon_\alpha \right) \right) \right. \\ & \left. \div (N_{oi} - \frac{v_{ii}}{v_{ii}} N_{oi} - \epsilon_i N_{or_i}) \right) = N \sum_{i=n_s+1}^{n_o} \left(\delta_{i\beta} - \frac{v_{ii}}{v_{ii}} \delta_{i\beta} - v_{ii} \epsilon_i (\delta_{\beta r_i} - M_{\beta i}) \right) \\ & \times \left[\delta_{i\gamma} - \frac{v_{ii}}{v_{ii}} \delta_{i\gamma} - v_{ii} \epsilon_i (\delta_{\gamma r_i} - M_{\gamma i}) \right] \div (-\epsilon_i N_{or_i}) \\ & = -N \sum_{i=n_s+1}^{n_o} \frac{v_{ii}^2 (\delta_{\beta r_i} - M_{\beta i}) (\delta_{\gamma r_i} - M_{\gamma i})}{N_{or_i}} \epsilon_i \quad (F-7) \end{aligned}$$

To take the limit of complete reactions, the limit as all the ϵ_i 's go to zero is taken on the right hand side of equation (F-7). This leads to the result that

$$(\underline{W}+\underline{K})^T \begin{pmatrix} \underline{0} & \underline{0} & \underline{0} \\ \underline{0} & \underline{X}_1^{-1} & \underline{0} \\ \underline{0} & \underline{0} & \underline{0} \end{pmatrix} (\underline{W}+\underline{K}) = \underline{0} \quad (\text{F-8})$$

in the limit of complete reactions.

APPENDIX G
ALTERNATIVE FORMULATION OF FLUCTUATION PROPERTIES FROM
INTEGRALS OF THE RADIAL DISTRIBUTION FUNCTION

Constraints on the Radial Distribution Function Integrals

Friedman and Ramanathan (1970) place the following constraints on the integrals of the radial distribution function, based on charge neutrality and material balance arguments:

$$(\underline{z})_{ik} + \sum_j (\underline{H})_{ij} x_j (\underline{z})_{jk} = 0 \quad 1 \leq i \leq n, \quad 1 \leq k \leq n - n_o \quad (G-1a)$$

or

$$(\underline{I} + \underline{H} \underline{X}) \underline{z} = \underline{0} \quad (G-1b)$$

There are two consequences of the presence of these constraints. The form of the constraints given in equation (G-1b) makes it clear that the relationship between \underline{A} and \underline{H} differs considerably from equation (4-23), in fact, it becomes a much simpler relationship. The form of equation (G-1a) shows that the models used for the $(\underline{H})_{ij}$ must be related to each other in this fashion. This implies that the constraints on the $(\underline{H})_{ij}$ may have to vary from system to system, particularly when common ions are involved. Examples of both of these effects are given below.

Equation (G-1b) can be used with equation (4-21) to give the following relationship between \underline{A} and \underline{H} :

$$\underline{A} = \underline{y}^T (\underline{X} + \underline{X} \underline{H} \underline{X}) \underline{y} \quad (G-2)$$

In terms of the desired quantities, this becomes

$$\underline{A}^{-1} = [\underline{y}^T (\underline{X} + \underline{X} \underline{H} \underline{X}) \underline{y}]^{-1} \quad (\text{G-3})$$

Although this is much simpler than equation (4-23) and its inverse, the need of a matrix inversion in equation (G-3) still makes determination of the elements of \underline{A} much more difficult in terms of the $(\underline{H})_{ij}$ than the $(\underline{C}^0)_{ij}$, and this difficulty increases greatly as the number of components increase.

Single-Salt, Single-Solvent System

In this simplest case, \underline{A} becomes

$$\begin{aligned} \underline{A} &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1/v_+ & 0 \end{pmatrix} \begin{pmatrix} x_{o1} + x_{o1}^2 (\underline{H})_{11} & x_{o1} x_+ (\underline{H})_{1+} & x_{o1} x_- (\underline{H})_{1-} \\ x_{o1} x_+ (\underline{H})_{1+} & x_+ + x_+^2 (\underline{H})_{++} & x_+ x_- (\underline{H})_{+-} \\ x_{o1} x_- (\underline{H})_{1-} & x_+ x_- (\underline{H})_{+-} & x_- + x_-^2 (\underline{H})_{--} \end{pmatrix} \begin{pmatrix} 0 & 0 \\ 0 & 1/v_+ \\ 0 & 0 \end{pmatrix} \\ &= \begin{pmatrix} x_{o1} + x_{o1}^2 (\underline{H})_{11} & x_{o1} x_{o2} (\underline{H})_{1+} \\ x_{o1} x_{o2} (\underline{H})_{1+} & \frac{x_{o2}}{v_+} + x_{o2}^2 (\underline{H})_{++} \end{pmatrix} \quad (\text{G-4}) \end{aligned}$$

Equation (G-1a) shows that

$$(\underline{H})_{1-} = (\underline{H})_{1+} \quad (\text{G-5a})$$

$$(\underline{H})_{+-} = \frac{1}{v_- x_{o2}} + (\underline{H})_{--} = \frac{1}{v_+ x_{o2}} + (\underline{H})_{++} \quad (\text{G-5b})$$

which indicates that equation (G-4) could be written in terms of the - ion with equivalent results, as required. For simplicity, we will use equation (G-5b) to write \underline{A} in terms of $(\underline{H})_{+-}$ instead of $(\underline{H})_{++}$.

The component fluctuation derivatives in terms of the $(\underline{H})_{ij}$ are
(compare equations 4-55 to 4-57)

$$\left. \frac{N}{kT} \frac{\partial \mu_{o1}}{\partial N_{o1}} \right|_{T,V,N_{o2}} = (\underline{A})_{11}^{-1} = x_{o2}^2 (\underline{H})_{+-} / \det(\underline{A}) \quad (G-6a)$$

$$\begin{aligned} \left. \frac{N}{kT} \frac{\partial \mu_{o1}}{\partial N_{o2}} \right|_{T,V,N_{o1}} &= \left. \frac{N}{kT} \frac{\partial \mu_{o2}}{\partial N_{o1}} \right|_{T,V,N_{o2}} = (\underline{A})_{12}^{-1} = (\underline{A})_{21}^{-1} \\ &= -x_{o1} x_{o2} (\underline{H})_{1+} / \det(\underline{A}) \end{aligned} \quad (G-6b)$$

$$\left. \frac{N}{kT} \frac{\partial \mu_{o2}}{\partial N_{o2}} \right|_{T,V,N_{o1}} = (\underline{A})_{22}^{-1} = [x_{o1} + x_{o1}^2 (\underline{H})_{11}] / \det(\underline{A}) \quad (G-6c)$$

where

$$\det(\underline{A}) = x_{o1} x_{o2}^2 (\underline{H})_{+-} + x_{o1}^2 x_{o2}^2 [(\underline{H})_{11} (\underline{H})_{+-} - (\underline{H})_{1+}^2] \quad (G-7)$$

Double-Salt, Single-Solvent System

Referring to equations (4-72) and (G-3), we have

$$\underline{A} = \begin{pmatrix} x_{o1} + x_{o1}^2 (\underline{H})_{11} & x_{o1} x_{o2} (\underline{H})_{12+} & x_{o1} x_{o3} (\underline{H})_{13+} \\ x_{o1} x_{o2} (\underline{H})_{12+} & \frac{x_{o2}}{v_{2+}} + x_{o2}^2 (\underline{H})_{2+2+} & x_{o2} x_{o3} (\underline{H})_{2+3+} \\ x_{o1} x_{o3} (\underline{H})_{13+} & x_{o2} x_{o3} (\underline{H})_{2+3+} & \frac{x_{o3}}{v_{3+}} + x_{o3}^2 (\underline{H})_{3+3+} \end{pmatrix} \quad (G-8)$$

where, from equation (G-1a),

$$(\underline{H})_{12-} = (\underline{H})_{12+} \quad (G-9a)$$

$$(\underline{H})_{13-} = (\underline{H})_{13+} \quad (G-9b)$$

$$(\underline{H})_{2+2-} = \frac{1}{v_{2-}x_{o2}} + (\underline{H})_{2-2-} = \frac{1}{v_{2+}x_{o2}} + (\underline{H})_{2+2+} \quad (G-9c)$$

$$(\underline{H})_{3+3-} = \frac{1}{v_{3-}x_{o3}} + (\underline{H})_{3-3-} = \frac{1}{v_{3+}x_{o3}} + (\underline{H})_{3+3+} \quad (G-9d)$$

$$(\underline{H})_{2+3+} = (\underline{H})_{2-3+} = (\underline{H})_{2+3-} = (\underline{H})_{2-3-} \quad (G-9e)$$

Rewriting \underline{A} in terms of $(\underline{H})_{2+2-}$, and $(\underline{H})_{3+3-}$ gives

$$\underline{A} = \begin{pmatrix} x_{o1} + x_{o1}^2 (\underline{H})_{11} & x_{o1}x_{o2} (\underline{H})_{12+} & x_{o1}x_{o3} (\underline{H})_{13+} \\ x_{o1}x_{o2} (\underline{H})_{12+} & x_{o2}^2 (\underline{H})_{2+2-} & x_{o2}x_{o3} (\underline{H})_{2+3+} \\ x_{o1}x_{o3} (\underline{H})_{13+} & x_{o2}x_{o3} (\underline{H})_{2+3+} & x_{o3}^2 (\underline{H})_{3+3-} \end{pmatrix} \quad (G-10)$$

Finally, the component fluctuation properties are (compare equations 4-73 to 4-78)

$$\left. \frac{N}{kT} \frac{\partial \mu_{o1}}{\partial N_{o1}} \right|_{T,V,N_{o2},N_{o3}} = x_{o2}^2 x_{o3}^2 [(\underline{H})_{2+2-} (\underline{H})_{3+3-} - (\underline{H})_{2+3+}^2] / \det(\underline{A}) \quad (G-11a)$$

$$\left. \frac{N}{kT} \frac{\partial \mu_{o1}}{\partial N_{o2}} \right|_{T,V,N_{o1},N_{o3}} = x_{o1}x_{o2}x_{o3}^2 [(\underline{H})_{2+3+} (\underline{H})_{13+} - (\underline{H})_{12+} (\underline{H})_{3+3-}] / \det(\underline{A}) \quad (G-11b)$$

$$\left. \frac{N}{kT} \frac{\partial \mu_{o2}}{\partial N_{o2}} \right|_{T,V,N_{o1},N_{o3}} = \left[x_{o1}x_{o3}^2 (\underline{H})_{3+3-} + x_{o1}^2 x_{o3}^2 [(\underline{H})_{11} (\underline{H})_{3+3-} - (\underline{H})_{13+}^2] \right] \div \det(\underline{A}) \quad (G-11c)$$

$$\left. \frac{N}{kT} \frac{\partial \mu_{o2}}{\partial N_{o3}} \right|_{T,V,N_{o1},N_{o2}} = \left[x_{o1}^2 x_{o2}x_{o3} [(\underline{H})_{12+} (\underline{H})_{13+} - (\underline{H})_{2+3+} (\underline{H})_{11}] - x_{o1}x_{o2}x_{o3} (\underline{H})_{2+3+} \right] \div \det(\underline{A}) \quad (G-11d)$$

where

$$\det(\underline{A}) = x_{o1}^2 x_{o2}^2 x_{o3}^2 [(\underline{H})_{2+2-} (\underline{H})_{3+3-} - (\underline{H})_{2+3+}^2] + x_{o1}^2 x_{o2}^2 x_{o3}^2 [(\underline{H})_{11} (\underline{H})_{2+2-}$$

$$\times (\underline{H})_{2+3+} - (\underline{H})_{13+}^2 (\underline{H})_{2+2-} - (\underline{H})_{2+3+}^2 (\underline{H})_{11-} - (\underline{H})_{12+}^2 (\underline{H})_{3+3-}]$$

In the above equations, the remaining derivatives of the chemical potential may be found by a simple exchange of subscripts 2 and 3.

Double-Salt, Single-Solvent System with Common Ion

In this system, \underline{A} can be determined from equations (G-2) and (4-95). Here, \underline{A} is found to be identical to that of the previous system (equation G-8). Now, however, the \underline{z} matrix (equation 4-96) differs, leading to:

$$(\underline{H})_{1-} = (v_{2-x_{o2}} + v_{3-x_{o3}})^{-1} [v_{2-x_{o2}} (\underline{H})_{12+} + v_{3-x_{o3}} (\underline{H})_{13+}] \quad (G-12a)$$

$$(\underline{H})_{2+-} = (v_{2-x_{o2}} + v_{3-x_{o3}})^{-1} \left[\frac{v_{2-}}{v_{2+}} + v_{2-x_{o2}} (\underline{H})_{2+2+} + v_{3-x_{o3}} (\underline{H})_{2+3+} \right] \quad (G-12b)$$

$$(\underline{H})_{3+-} = (v_{2-x_{o2}} + v_{3-x_{o3}})^{-1} \left[\frac{v_{3-}}{v_{3+}} + v_{2-x_{o2}} (\underline{H})_{2+3+} + v_{3-x_{o3}} (\underline{H})_{3+3+} \right] \quad (G-12c)$$

$$\begin{aligned} (\underline{H})_{--} = & (v_{2-x_{o2}} + v_{3-x_{o3}})^{-1} \left[1 + \frac{v_{2-}^2}{v_{2+}} x_{o2} + \frac{v_{3-}^2}{v_{3+}} x_{o3} + v_{2-x_{o2}}^2 (\underline{H})_{2+2+} \right. \\ & \left. + 2v_{2-x_{o2}} v_{3-x_{o3}} (\underline{H})_{2+3+} + v_{3-x_{o3}}^2 (\underline{H})_{3+3+} \right] \quad (G-12d) \end{aligned}$$

As the limit to one salt is taken ($x_{o2} \rightarrow 0$ or $x_{o3} \rightarrow 0$), the above equations agree with equations (G-5), as expected. However, they do indicate that the interrelationship between the $(\underline{H})_{ij}$'s depends on the system of interest, so the $(\underline{H})_{ij}$ cannot be uniquely determined for two ions outside of the framework of the system. This difficulty again makes the direct correlation function integrals more attractive, despite the simplifications in the relationship of \underline{A} to \underline{H} (which are still much more complex than that of \underline{A} to \underline{C}^0).

APPENDIX H INDEPENDENCE OF SALTS

"Groups" of Salts

The simplest method to assure independence of the salts in a given electrolyte solution is to separate the salts into groups having the following properties:

- 1) every salt in a given group has an ion common to another salt in that group,
- 2) no salt in any group has an ion common to any salt in another group (this also means that each salt is in only one group),
- 3) the groups contain as few salts as possible,
- 4) salts with no ions common to other salts form single-salt groups.

An example is the system with the following \underline{v} matrix (ignoring the solvents which form their own groups), with seven different ions ($n=7$) in five salts ($n_o=5$).

$$\underline{v} = \begin{pmatrix} v_{1,1+} & 0 & 0 & v_{4,1+} & 0 \\ 0 & v_{2,2+} & v_{3,2+} & 0 & 0 \\ 0 & 0 & 0 & 0 & v_{5,3+} \\ v_{1,1-} & 0 & 0 & 0 & 0 \\ 0 & v_{2,2-} & 0 & 0 & 0 \\ 0 & 0 & v_{3,3-} & 0 & 0 \\ 0 & 0 & 0 & v_{4,4-} & v_{5,4-} \end{pmatrix}$$

We group the \underline{v} matrix according to the above rules so that salts 1,4,5 form group one and salts 2 and 3 form group two. Salts 1 and 4 have a common cation, 4 and 5 a common anion so all must be grouped together. Salts 1 and 5 are in the same group because if either 1,4 or 5 were placed in a third group, rule two would be violated. If a sixth salt were added, having no ions common to the other five salts, it would form a third group by rule four. The most complicated systems can easily be separated into groups by examining their \underline{v} matrices.

Tests for Independence

After the salts are grouped as suggested above, each group can be tested for independence of their salts. As a first test, if the number of salts in a group is greater than or equal to the number of ions in that group, the salts are not independent. For systems where each salt has only two kinds of ions (+ and -), each group must have exactly one more ion than salt for the salts to be independent.

Allowing for salts containing more than two kinds of ions yields a situation that is somewhat more complicated. In this case, it is possible to have fewer salts than ions and still have dependent salts. A test which can be used for each group is to see if a set of coefficients, R_α , can be found such that, in the sum over all salts in the group,

$$\sum_{\alpha} R_{\alpha} v_{i\alpha} = 0 \quad \text{for all } i=1,\dots,n \quad (\text{H-1})$$

Notice that $R_{\alpha} = 0$ if salt α has an ion that is not common to any other salt. Furthermore, if every salt has such a unique ion, the salts are

independent, but this is not a necessary condition. For example for the group where

$$\underline{v} = \begin{pmatrix} v_{1,1+} & 0 \\ v_{1,2+} & v_{2,2+} \\ v_{1,1-} & v_{2,1-} \end{pmatrix}$$

we see that salt 2 does not have a unique ion, but salts 1 and 2 are independent.

As an example of a dependent system where $n=n_0+1$, we take ($n=5$, $n_0=4$)

$$\underline{v} = \begin{pmatrix} v_{1,1+} & 0 & v_{3,1+} & 0 \\ v_{1,2+} & v_{2,2+} & 0 & 0 \\ 0 & v_{2,3+} & 0 & v_{4,3+} \\ v_{1,1-} & v_{2,1-} & 0 & 0 \\ 0 & 0 & v_{3,2-} & v_{4,2-} \end{pmatrix}$$

Since no salt has a unique ion, we must include all the salts in the summation of (H-1). Using the charge neutrality conditions on each salt,

$$\sum_i v_{i\alpha} z_i = 0 \quad \text{for all } \alpha=1, \dots, n_0,$$

we can indeed show that a set of R_α 's exists so that salts are dependent. In general, all distinct sets of R_α 's must be found (excluding simple multiples) and for all such sets, one salt must be eliminated as dependent. The choice for the salt to be eliminated can be found among

those which have no unique ions. This method is very similar to that used to determine independence of reactions (Denbigh, 1971, p. 169ff).

After each group of salts is reduced to independent salts as above, the constraint matrix, \underline{z} , can be determined.

APPENDIX I
ELECTROSTATIC EXPRESSIONS FOR MULTISALT SYSTEMS

Debye-Hueckel Limits

The formalism of Chapter 4 is directly applicable to a general system of multiple solvents and solvents. The Debye-Hueckel terms were given only for single solvent-single salt systems. Since we deal only with electrostatic effects, these terms can only be written for a single solvent, or in terms of a "pseudo-component" defined as the salt-free mixture of the solvents and designated below by the subscript 1. For such a system, the activity coefficient limits become

$$v_{\alpha} \ln \gamma_{\pm\alpha} = - S_{\gamma}^1 q_{\alpha} \left(\rho \sum_{\gamma=2}^{n_o} x_{o\gamma} q_{\gamma} \right)^{1/2} \quad (\text{I-1a})$$

where

$$S_{\gamma}^1 = \pi^{1/2} N_A^2 \left[\frac{e^2}{\epsilon_1 RT} \right]^{3/2} \quad (\text{I-1b})$$

$$q_{\alpha} = \sum_{i=2}^{n_o} v_{i\alpha} z_i^2 \quad (= 0 \text{ for solvent}) \quad (\text{I-1c})$$

These summations begin at 2 since we include only the salts, not solvents. The partial molar volumes become

$$\bar{v}_{o\alpha} - \bar{v}_{o\alpha}^{\infty} = \frac{3}{2} S_{\gamma}^1 q_{\alpha} \left(\rho \sum_{\gamma=2}^{n_o} x_{o\gamma} q_{\gamma} \right)^{1/2} \quad (\text{I-2a})$$

$$S_v^1 = S_Y^{1RT} \left\{ \frac{\partial \ln \epsilon_1}{\partial P} \right\}_T - \frac{\kappa_1}{3} \} \quad (I-2b)$$

Where $\bar{v}_{o\alpha}^\infty$ is the partial molar volume of salt α at infinite dilution in the solvent mixture. And the apparent compressibility becomes

$$\phi_k - \phi_k^o = \frac{2}{3} S_k^1 \left(\rho \sum_{Y=2}^{\infty} x_{oY} q_Y \right)^{1/2} \left(\sum_{Y=2}^{n_o} x_{oY} \right)^{1/2} \quad (I-3a)$$

where

$$S_k^1 = \frac{S_Y^{1RT}}{4} \left\{ \kappa_1^2 + 2 \frac{\partial \kappa_1}{\partial P} \right\}_T - 6 \kappa_1 \frac{\partial \ln \epsilon_1}{\partial P} \Big|_T + 9 \left(\frac{\partial \ln \epsilon_1}{\partial P} \right)_T^2 - 6 \frac{\partial^2 \ln \epsilon_1}{\partial P^2} \Big|_T \} \quad (I-3b)$$

The Debye-Hueckel limits to the direct correlation function integrals become:

$$\begin{aligned} 1-C_{11}^o &= \frac{1}{\rho_1 \kappa_1 RT} \left(1 + \sum_{Y=2}^{n_o} v_Y x_{oY} \right) - \frac{\phi_k^o}{\kappa_1^2 RT} \left(\sum_Y v_Y x_{oY} \right) \\ &- \left\{ \frac{S_v^1}{\kappa_1 RT} + \frac{S_Y^1}{2} + \frac{2}{3} \frac{S_k^1}{\kappa_1^2 RT} \right\} \rho_1^{1/2} \left(\sum_{Y=2}^{n_o} x_{oY} q_Y \right)^{3/2} \end{aligned} \quad (I-4a)$$

$$1-C_{1\alpha}^o = \frac{\bar{v}_{o\alpha}^\infty}{v_\alpha \kappa_1 RT} + \frac{3}{2} \frac{S_Y^1}{v_\alpha \kappa_1} \frac{\partial \ln \epsilon_1}{\partial P} \Big|_T q_\alpha \rho_1^{1/2} \left(\sum_{Y=2}^{n_o} x_{oY} q_Y \right)^{1/2} \quad (I-4b)$$

and

$$1-C_{\alpha\beta}^o = - \frac{S_Y^1 q_\alpha q_\beta \rho_1^{1/2}}{n_o} \frac{2 v_\alpha v_\beta \left(\sum_{Y=2}^{n_o} x_{oY} q_Y \right)^{1/2}}{\quad} \quad (I-4c)$$

Mean Spherical Model Expansion

As described in Chapter 5, a half-power expansion in salt density derived from the Mean Spherical Model is used to improve the Debye-Hueckel approximation for the ion-ion direct correlation function integral. The equations for these terms are given in Chapter 5 also. However, actual calculation of properties requires integration of these terms over composition and pressure. The composition integrations of the Debye-Hueckel terms are straightforward, but this is not the case for the expanded terms of the Mean Spherical Model. Therefore, the salt-density expansion of the activity coefficient of salt α , including the Debye-Hueckel portion, is given below

$$v_{\alpha} \ln \gamma_{\pm\alpha} = -S_{\gamma}^1 q_{\alpha} \left(\rho \sum_{\gamma=2}^n x_{o\gamma} q_{\gamma} \right)^{1/2} + \alpha^2 \sum_{i=1}^n v_{i\alpha} z_i^2 \sum_{k=1}^{\infty} B_{ik}(\sigma_i, \eta) \kappa^k \quad (\text{I-5})$$

where σ_i , η_k and α^2 are defined in Chapter 5, and κ is the inverse Debye length. The B_{ik} 's are as follows:

$$B_{i1} = a_1(\sigma_i + \eta_1)$$

$$B_{i2} = a_2(2\sigma_i + \frac{1}{2}\eta_1) + \frac{2}{3}b_2(\sigma_i^2 + \frac{3}{2}\eta_2)$$

$$B_{i3} = \frac{1}{2}a_3(\sigma_i \eta_1^2) + b_3(\sigma_i \eta_2 + \sigma_i^2 \eta_1 + \eta_1 \eta_2) + \frac{1}{2}c_3(\sigma_i^3 + 2\eta_3)$$

$$B_{i4} = a_4(\eta_1^3)(4\sigma_i - \frac{1}{2}\eta_1) + b_4(\eta_1)(2\sigma_i \eta_2 + \sigma_i^2 \eta_1 + \frac{1}{2}\eta_1 \eta_2) \\ + c_4(\sigma_i \eta_3 + \sigma_i^3 \eta_1 + \frac{3}{2}\eta_1 \eta_2) + d_4(\eta_4)(2\sigma_i^2 + \frac{3}{2}\eta_2) + e_4(\sigma_i^4 + \frac{5}{2}\eta_4)$$

The a_i 's, b_i 's, c_i 's, d_4 and e_4 are fitted parameters and are identical to those used for the direct correlation function integrals.

APPENDIX J
HARD-SPHERE FORMULAE

Hard-Sphere Terms for Direct Correlation Function Integrals

The hard-sphere contribution to the direct correlation function integrals can be derived from the mixture form of the Carnahan-Starling equation of state (Mansoori, et al., 1970). For two species (not components) i and j in solution, we have

$$\begin{aligned}
 -\frac{(\bar{C}^o)_{ij}^{hs}}{\zeta_o} = & \frac{(\sigma_i + \sigma_j)^3}{1 - \zeta_3} + \{3\sigma_i \sigma_j \zeta_2 [(\sigma_i + \sigma_j)^2 + \sigma_i \sigma_j] + 3\zeta_1 (\sigma_i \sigma_j)^2 (\sigma_i + \sigma_j) \\
 & + \zeta_o (\sigma_i \sigma_j)^3\} / (1 - \zeta_3)^2 + 9(\sigma_i \sigma_j \zeta_2)^3 / (1 - \zeta_3)^4 \\
 & + \frac{\zeta_2 (\sigma_i \sigma_j)^2}{(1 - \zeta_3)^3} \{9\zeta_2 (\sigma_i + \sigma_j) + 6\zeta_1 \sigma_i \sigma_j + [6 + \zeta_3 (-15 + 9\zeta_3)] / \zeta_3 \\
 & - (\sigma_i + \sigma_j) \zeta_2 [6 + \zeta_3 (-15 + 12\zeta_3)] / \zeta_3^2 + \zeta_2^2 \sigma_i \sigma_j [6 + \zeta_3 (-21 + \zeta_3 \times \\
 & (26 - 14\zeta_3))] / \zeta_3^2 (1 - \zeta_3)\} + 6\zeta_2 (\sigma_i \sigma_j)^2 \ln(1 - \zeta_3) \\
 & \times \{\zeta_3 - (\sigma_i + \sigma_j) \zeta_2 + \zeta_2^2 \sigma_i \sigma_j / \zeta_3\} / \zeta_3^3
 \end{aligned} \tag{J-1a}$$

where

$$\zeta_k = \frac{\pi}{6} \sum_i \rho_i \sigma_i^k \tag{J-1b}$$

The component functions are, of course

$$C_{\beta\alpha}^{hs} = \sum_i \sum_j v_{i\alpha} v_{j\beta} (C_{ij}^o)^{hs} / v_{\alpha} v_{\beta} \quad (J-2)$$

Unfortunately, the infinite dilution limits of these correlation functions are not correct, so the model must be altered to account for this deficiency. This accounting is given in Chapter 5, where the following notation is used. These correction terms are used only in the solvent-solvent and solvent-ion direct correlation function integrals. If we allow s to denote the solvent pseudo-component and γ the salts, we have

$$C_{ss}^{hso} = \lim_{\{x_{o\gamma}\} \rightarrow 0} C_{ss}^{hs} \quad (J-2a)$$

$$C_{ss}^{hs'} = \lim_{\{x_{o\gamma}\} \rightarrow 0} \sum_{\gamma}^{\text{salts}} \left. \frac{\partial C_{o\gamma}^{hs}}{\partial x_{o\gamma}} \right|_{T, x_{o\beta} \neq \gamma} \quad (J-2b)$$

As a work of explanation, these are limits as the total salt concentration goes to zero while the salt-free solvent composition is held constant. We also define $C_{s\alpha}^{hso}$ similarly to C_{ss}^{hso} in equation (J-2a).

Finally, the hard-sphere contribution to the activity coefficient is given by,

$$\begin{aligned} \ln \gamma_i = & -\ln(1-\zeta_3) \left[1 - 3 \left(\frac{\zeta_{2i}^{\sigma}}{\zeta_3} \right)^2 + 2 \left(\frac{\zeta_{2i}^{\sigma}}{\zeta_3} \right)^3 \right] \\ & + \frac{1}{1-\zeta_3} \left[\zeta_{o\sigma i}^3 + 3\zeta_{2\sigma i}^{\sigma} + 3\zeta_{1\sigma i}^2 + 3\zeta_3 \left(\frac{\zeta_{2i}^{\sigma}}{\zeta_3} \right)^2 - \zeta_3(2-\zeta_3) \left(\frac{\zeta_{2i}^{\sigma}}{\zeta_3} \right)^3 \right] \end{aligned}$$

$$\begin{aligned}
& + \frac{1}{(1-\zeta_3)^2} \left[3\zeta_1\zeta_2\sigma_i^3 + \frac{9}{2}\zeta_2^2\sigma_i^2 - \frac{3}{2}\zeta_3^2\left(\frac{\zeta_2\sigma_i}{\zeta_3}\right)^2 \right] \\
& + \frac{1}{(1-\zeta_3)^3} \left[3\zeta_2^3\sigma_i^3 - \zeta_3\zeta_2^3\sigma_i^3 \right]
\end{aligned} \tag{J-3}$$

Again, this is for a species and not a component. For components, we use

$$\ln\gamma_{o\alpha} = \sum_{i=1}^n v_{i\alpha} \ln\gamma_i \tag{J-4}$$

This expression is the analytic integration of the $C_{\alpha\beta}^{hs}$'s, which, of course, for our calculations are integrated from a reference state $(T, \rho^r, \underline{x}_0^r)$. When we integrate over all the member densities to T, ρ, \underline{x}_0 we get simply,

$$\ln\gamma_{o\alpha}(T, \rho, \underline{x}_0) - \ln\gamma_{o\alpha}(T, \rho^r, \underline{x}_0^r)$$

which is much easier to evaluate than the multiple integrations of the C^{hs}_s .

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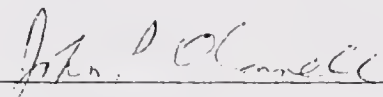
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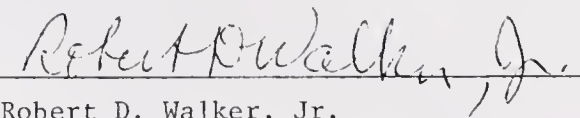
BIOGRAPHICAL SKETCH

Randal L. Perry was born in Wilmington, Delaware, on July 4, 1955. In June of 1972, he graduated from the Coatesville Area Senior High School in Coatesville, Pennsylvania. Seeking warmer weather, he enrolled at Rice University in Houston, Texas, in August, 1972, and received his Bachelor of Science in Chemical Engineering degree, magna cum laude, in May, 1976. While an undergraduate, he was elected to Tau Beta Pi and Phi Beta Kappa. After a summer working for the Dupont Corporation, he began graduate school at the University of Florida in Gainesville, Florida. There, he received his Master of Science degree in August of 1977 and expects to receive his Doctor of Philosophy degree in December of 1980, both in chemical engineering. Additionally, he was enrolled in the chemical physics option. Presently, he is an Assistant Professor of Chemical Engineering at the University of Virginia in Charlottesville, Virginia.

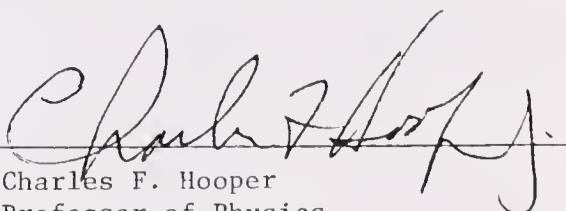
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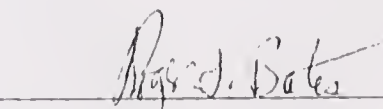
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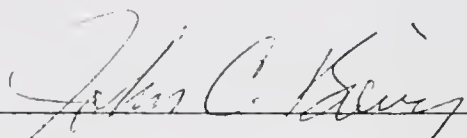
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Roger Bates
Professor of Chemistry

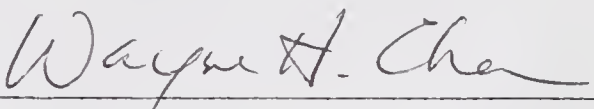
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This dissertation was submitted to the Graduate Faculty of the College of Engineering and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December, 1980



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